TTP AND TTT DIAGRAMS FOR QUENCH SENSITIVITY OF 6013 ALLOY.

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ABSTRACT Quench sensitivity TTP and TTT diagrams of 6013 alloy within temperature interval 250–500°C were obtained. Solid solution decomposition kinetics were determined by electroconductivity and tensile properties measurements. Phase transformations have been investigated using high sensitive X-ray phase analysis, TEM, SEM and DSC. Cooling rate enough to suppress solid solution decomposition on quenching estimated by 95 % UTS criteria is equal to ~25 °C/s. At temperatures between solvus and 500 °C only β phase (Mg_2Si) with a cubic structure of CaF_2 type exists. In temperature interval 400–500 °C two phases were found – β phase and hexagonal Q phase ($Al_5Cu_2Mg_8Si_6$). In temperature interval 250–400 °C mainly Q phase was observed. At lower temperatures 250–325 °C intermediate Q′ phase was found.

Keywords: *TTP and TTT diagrams, quench sensitivity, 6013 alloy, β phase (Mg_2Si), Q phase ($Al_5Cu_2Mg_8Si_6$), electroconductivity, tensile properties.*

1. INTRODUCTION

Al-Mg-Si-(Cu) 6013 alloy is perspective for wide application in an aircraft industry as it has an attractive combination of medium strength with good plasticity, formability, fracture toughness, corrosion resistance and weldability [1,2]. TTP and TTT diagrams in quenching sensitivity temperature interval represent a large interest for the alloy nature understanding and for correct choice of SST and quenching regimes [3, 4]. Two equilibrium phases are known in Al-Mg-Si-(Cu) system: β phase (Mg_2Si) with a cubic Fm3m structure of CaF_2 type (a = 0.639 nm) and hexagonal Q phase ($Al_5Cu_2Mg_8Si_6$) (a = 1.032 nm, c = 0.405 nm) [5, 6]. Intermediate phases forming during solid solution decomposition in low temperature interval are GP zones, β″ and β′ phases. Their crystal structure is under discussion [7–15].

TTP quench sensitivity diagrams for the several Russian alloys basing on the 95 % UTS measurements were obtained in [3] and electroconductivity TTP diagram for Al-Mg-Si 6063 alloy was presented in [7]. We didn't find any published TTT diagrams for quench sensitivity temperature interval for Al-Mg-Si-(Cu) alloys based on the structure studies results (TEM, X-ray phase analysis, etc.). In Al-1 % Mg_2Si alloy [8] β″ phase precipitation was discovered by TEM after direct annealing 550 °C → 180 °C, 72 h. After direct annealing 550 °C → 350 °C, 2 h heterogeneous β′ phase precipitation on dislocations was observed. More prolonged annealing 550 °C → 350 °C, 44 h led to β′ phase dissolution whereas β phase plates grew. After direct annealing 550 °C → 450 °C, 2 h only β phase plates were found. The goal of the present work was to obtain TTP and TTT diagrams for quench sensitivity temperature interval of 6013 alloy.

2. EXPERIMENTAL

The study was carried out on the industrial 1.6 mm sheets of 6013 alloy. Chemical composition of 6013 alloy is presented in Table 1.

Table 1. Alloy 6013 chemical composition.

	Cu	Mg	Mn	Si	Fe	Zn	Ti	Cr	Be	Zr
wt. %	0.6	0.83	0.29	0.71	0.21	0.1	0.03	0.05	0.0008	0.05

Sheet cards were solution treated at 565 °C, water quenched and stretched for a small degree followed by a prolonged natural ageing (as-received temper). Standard heat treatment procedure for TTT and TTP diagrams is a solid solution treatment (SST) followed by a quenching into preheated liquid media and subsequent annealing for required time (direct annealing). The scheme of laboratory heat treatment unit, which was used in this work, is given in Fig. 1. In distinction to quenching into liquid media this unit allows to control cooling rate in different temperature intervals.

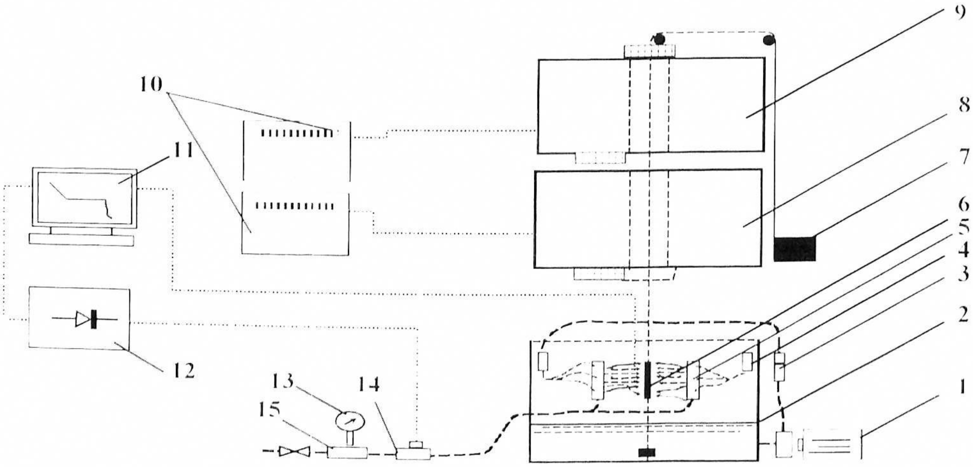


Fig. 1. Laboratory heat treatment unit.

1. Water pump 2. Water tank 3. Water pressure gauge 4. Water distributive unit 5. Injector 6. Mobile specimen carriage 7. Carriage handle 8. Air circulating furnace for SST 9. Air circulating furnace for isothermal annealing 10. Furnace temperature control device 11. Computer for recording of the specimen temperature 12. Thyristor converter 13. Air pressure gauge 14. Compressed air valve 15. Air flow gate

The unit consists of two co-axis air circulating through-type furnaces (8) and (9), in which furnace (8) is used for solution treatment, furnace (9) – for isothermal heat treatment. The block of water-air cooling (5) include 12 injectors which are joined into 4 groups by three injectors. The specimen is fixed on movable carriage (6), which moves by handle (7). Thermocouples (from one up to three) are inserted into a specimen. Thermocouples signals are transformed by analog-to-digital converter and then are recorded by the computer (11). Cooling can be interrupted at predefined temperature. Immediately after that the specimen carriage is moved into furnace (9) and is exposed for required time followed by the water quenching. The cooling rate down to a given annealing temperature is equal to 50-60 °C/s. Annealing temperature variations didn't exceeds ±5 °C. Direct annealing was carried out on samples 180x30x1.6 mm in size, cut out along rolling direction. Then electroconductivity γ was measured. After that samples were cut into four equal parts. One part was used for structural investigations, three others – for tensile tests. These samples were aged by the standard for 6013 alloy regime: 190 °C, 4 h.

Electroconductivity. γ values were measured by edge current method with the accuracy of ±0.3 MSm/m. High sensitivity X-ray phase analysis was performed with Debue camera in monochromatic CrK$_\alpha$ radiation. X-ray lines identification was carried out using calculated debuegrams with Al reference lines [9]. Estimation of the method sensitivity gives ~0.1 vol %. Thin films for TEM were prepared by double-jet elecropolishing method in the electrolyte 30 % HNO_3 – CH_3OH cooled down to –20 °C and then examined in JEM 100CX transmission electron microscope. DSC curves were registered on the SETARAM DSC-111 calorimeter at heating rate of 2 and 5 °C/min in the temperature intervals (20-350)°C and (20-600)°C in an aluminium crucible in He atmosphere.

3. RESULTS AND DISCUSSION

Measured Υ values are presented on the diagram (Fig. 2), UTS and YS measurements — on the diagrams (Fig. 3). After cooling with a rate — 50:60°C in a wide temperature interval (275-400)°C Υ, UTS and YS are changed after 1-4 s, that indicates to the high quench sensitivity of 6013 alloy. Cooling rate enough to suppress solid solution decomposition estimated by 95 % UTS criteria is equal to ~ 25 °C/s. Temperature interval of the minimal solid solution stability is (325-400)°C. At temperatures of ~ (375-400) and 300°C solid solution decomposition completed earlier than in other intervals. This indicates to different phase composition in these temperature intervals since each phase has its own C curve.

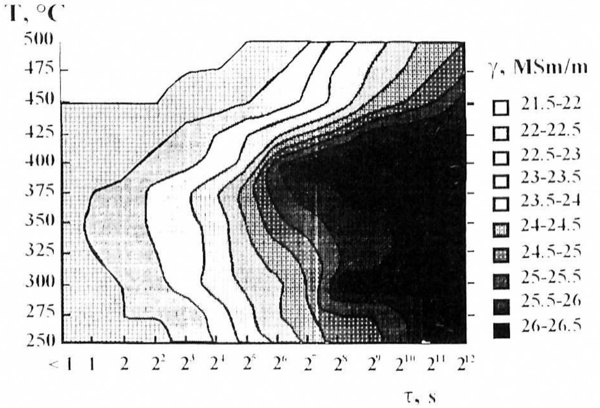
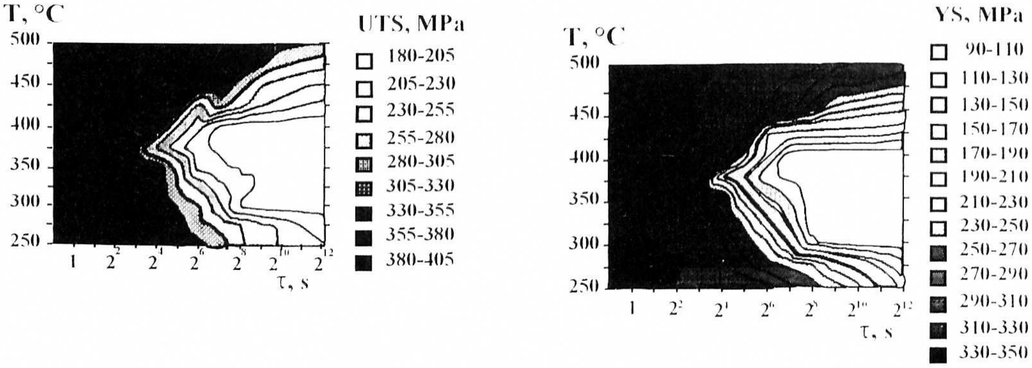


Fig 2. TTP diagram plotted on the basis of electroconductivity measurements.

The light microscopy and EDX examinations showed that direct annealing at 500°C caused heterogeneous nucleation of plate-shaped Mg- and Si-containing particles on the large Fe-containing particles and on dispersoids. At this temperature X-ray phase analysis detects lines of β phase (Mg_2Si) and several additional lines, belonging to Q phase ($Al_5Cu_2Mg_8Si_6$) (Table 2). The intensity of the most high-temperature DSC peak is increased in compare to as-received temper (Fig. 4). All these data indicates that β phase is the dominant phase on direct annealing at 500°C and high temperature peak on a DSC curve is a peak of β phase dissolution. After direct annealing 450°C, 1 h large particles inside grains and on grain boundaries were observed. X-ray phase analysis indicated the presence of a large amount of β phase. In a whole temperature interval (250-500)°C additional X-ray lines were observed. They cannot be explained basing the β′ lattice [9-14]. The best fit between experimental and calculated d/n values was obtained for Q phase and C phase [15] with the same crystal structure. When temperature decreased down to 400°C additional precipitates nucleated within grains. Their size was order of magnitude less than the size of coarse particles at 450°C. EDS spectra indicates the presence of Mg, Si and Cu in these precipitates. TEM results are presented in Fig. 5. SADP analysis shows the presence of hpc phase with periods **a** = 1.035 nm and **c** = 0.405 nm (Fig. 6). Its lattice is the same as the lattice of equilibrium Q phase. Period **c** is equal to matrix period, so this phase may be coherent with matrix (orientation relationship $[001]_Q \parallel [001]_{Al}$). Similar structures were described in aged Cu-containing 6061 alloy [16] and in Al-Mg_2Si with excess of Si [15]. These facts indicate the similarity of Q and β′ phases crystal structures.

After direct annealing at 450°C and 425°C kink appears on the dissolution DSC peak at (350-500)°C. This effect may be explained by increasing of Q phase volume fraction. Q phase dissolves in temperature interval ~(400-510)°C, β phase — ~(480-560)°C (Fig. 4). X-ray analysis shows that Q phase dominates in (375-250)°C temperature interval. Particles spatial density increased. Analysis of SADP supports the presence of Q phase in case of direct annealing 275°C. At the same time thin lath-shaped particles were observed in temperature interval (250–325)°C. Their diffraction patterns were closed to β′ ones [9–14], but several distinctions were found. Their sections were the same as for particles in [17], where solid solution decomposition in Cu-containing and Cu- free alloys was studied and precipitates

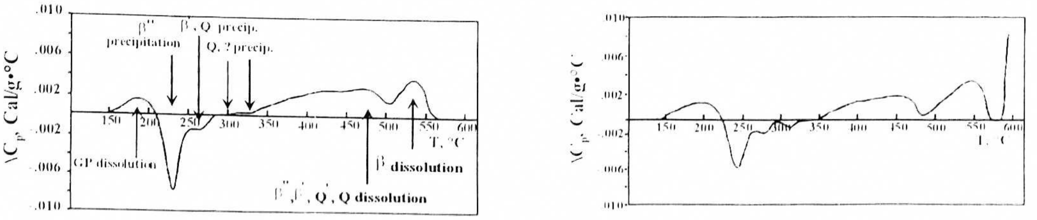


a b

Fig. 3. TTP diagrams, plotted on the base of UTS (*a*) and YS (*b*)

Table 2. Additional lines on X-ray photographs.

d (experim.), nm	Q phase, hcp, a=1.035 nm, c=0.405 nm		B phase [9], hcp, a=0.705 nm, c=0.405 nm	
	d	hkl	d	hkl
0.298	0.300	201, 300	—	
0.281	—	—	0.283	210
0.258	0.259	420	0.259	220
0.247	0.248	410	0.248	111
0.185	0.185	202	0.186	231
0.152	0.150	402	0.151	302
0.140	0.141, 0.140	512, 601	0.141, 0.140	322, 341



a b

Fig. 4. DSC curve of 6013 alloy sheet sample (a) in as-received temper, (b) after direct annealing 500 °C, 1 h

were laths (not rods). Special X-ray investigation of Al-0.83 Mg-0.62 Si - 2.1 Cu (in wt %) alloy (monocrystal, monochromatic MoK$_\alpha$ radiation) detected particular additional diffuse rods along $[100]^*_{Al}$, distinctive from diffuse scattering from Θ″ and β″ phases. The same scattering was found on the SADP in 6013 alloy after direct annealing at temperatures (250–300)°C. That's why we identify this phase as Q′ phase — metastable precursor of equilibrium Q phase — close to β′ phase but having its own crystal structure. DSC curves analysis showed that direct annealing (250–350)°C, 1 h caused the complete solid solution decomposition. TTT diagram for quench sensitivity temperature interval obtained basing on the above results is shown in Fig. 7.

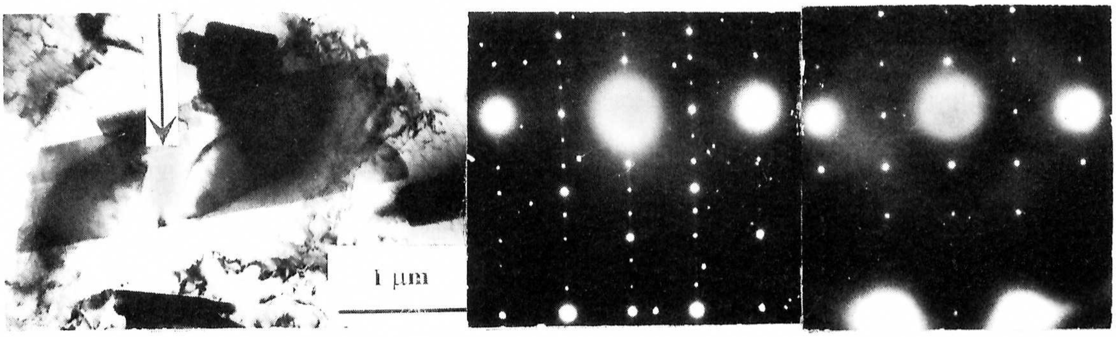


Fig. 5. TEM light field image and SADP of Q phase particle. Direct annealing 400°C, 5 min.

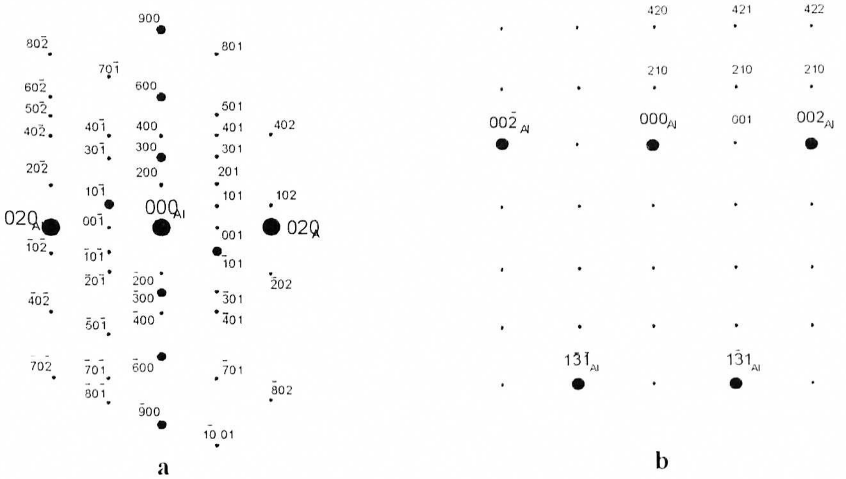


Fig. 6. SADP schemes for Fig. 5. (a) — $(010)^*_Q$, (b) — $(1\ \bar{2}0)^*_Q || (310)^*_{Al}$.

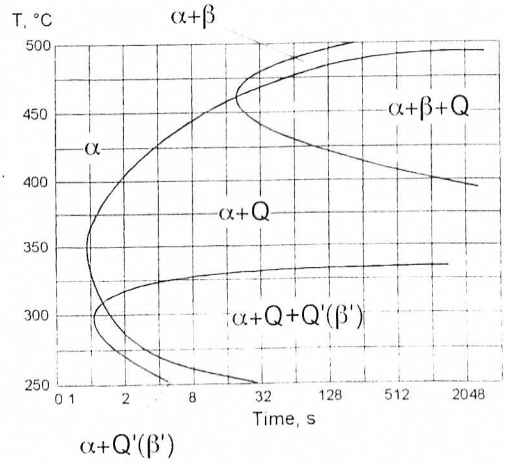


Fig. 7. TTT diagram for quench sensitivity temperature interval of 6013 alloy

4. CONCLUSIONS

1. Electroconductivity, UTS and YS TTP diagrams for quench sensitivity temperature interval of 6013 alloy were obtained. Cooling rate enough to suppress solid solution decomposition estimated by 95 % UTS criteria is equal to ~ 25 °C/s. Temperature interval of the minimal solid solution stability is (325 – 400) °C. At temperatures of ~ (375 – 400) and 300 °C solid solution decomposition completes earlier than in other intervals.

2. On the basis of X-ray phase analysis, TEM, SEM and DSC techniques TTT diagram for 6013 alloy in quench sensitivity temperature interval was obtained. After direct annealing two equilibrium phases — β phase (Mg_2Si) with a cubic structure of CaF_2 type and hexagonal Q phase ($Al_5Cu_2Mg_8Si_6$) — were determined. At temperatures between solvus and ~500 °C only β phase exists. In temperature interval (400–500)°C both β and Q phase were found. In temperature interval (250–400)°C mainly Q phase was observed. At lower temperatures (250–325) °C intermediate Q' phase appeared. For these phases morphology, orientation relationships and specific diffraction effects were established.

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