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KINETICS OF DECOMPOSITION OF THE SOLID SOLUTION OF SCANDIUM IN ALUMINUM IN BINARY Al – Sc ALLOYS

V. V. Zakharov¹Translated from *Metallovedenie i Termicheskaya Obrabotka Metallov*, No. 7, pp. 44 – 48, July, 2015.

C-curves of isothermal decomposition of the solid solution of scandium in aluminum are plotted for binary Al – Sc alloys with different scandium content. It is shown that growth in the scandium content from 0.14 to 0.55% reduces the incubation period by 2 – 3 orders of magnitude and increases the rate of the decomposition by 2 orders of magnitude. The causes of the accelerated decomposition of the solid solution of scandium in aluminum are discussed.

Key words: alloys of the Al – Sc system, concentration and kinetics of decomposition of solid solution.

INTRODUCTION

The high interest of researches in scandium as an alloying component of aluminum alloys is chiefly connected with its strong hardening action. A low additive of scandium raises the strength characteristics of some aluminum alloys to 200 MPa. Scandium is also a very strong modifier of the cast grain structure of aluminum alloys and thus improves their castability and weldability. The nature of the effect of scandium on the structure and properties of aluminum alloys is similar to that of other already widely used alloying components of transition metals, such as manganese, chromium and zirconium.

In continuous casting of ingots a part of scandium (which is comparatively low) is precipitated during the crystallization process from the aluminum melt in the form of numerous fine particles of Al₃Sc that are effective centers of crystallization of grains of the aluminum solid solution.

A larger part of the introduced scandium gets into the solid solution, which decomposes under the subsequent process heating required for transforming the ingots into deformed semiproducts. The products of the decomposition are particles of an equilibrium Al₃Sc phase that are dispersed in the initial stages of the decomposition. These nanoparticles 5 – 10 nm in size with a high density of distribution in the aluminum matrix cause strong hardening. When the decom-

position develops, the particles coagulate, and the distance between them increases. The hardening effect is decreased, but the anti-recrystallization action of the particles is preserved for a long time. The products of the decomposition of the solid solution of scandium in aluminum affect strongly the structure and properties of the aluminum alloy.

We presume that any information that characterizes the decomposition of the solid solution of scandium in aluminum, especially the kinetics of the decomposition, is not only interesting but also important from the standpoint of practice.

It has been shown in [1] that the decomposition of the solid solution of scandium in aluminum develops at a high rate that exceeds considerably the rate of the decomposition of solid solutions of other transition metals in aluminum.

Particles of a new Al₃Sc phase forming upon the decomposition of the solid solution of scandium in aluminum nucleate easily in the aluminum matrix due to the unique size and structural similarity of their crystal lattices. For this reason, the particles precipitate in the form of an equilibrium Al₃Sc phase (without metastable stages) fully coherent to the aluminum matrix. The activation energy of the process of the nucleation of particles of Al₃Sc is several times lower than the activation energy of the decomposition of the solid solutions of other transition metals in aluminum.

The aim of the present work was to study the kinetics of the decomposition of the solid solution of scandium in aluminum in binary Al – Sc alloys with different contents of scandium.

¹ All-Russia Institute of Light Alloys (VILS), Moscow, Russia (e-mail: zakharov_valery@mail.ru).

METHODS OF STUDY

We used continuous casting to obtain ingots 92 mm in diameter from binary Al – Sc alloys with different scandium content. The actual content of scandium in the ingots was 0, 0.14, 0.23, 0.35, 0.40 and 0.55 wt.%. The admixtures were 0.02% Fe, 0.01% Si and 0.06% Ti. The temperature, time, and rate modes of melting and casting of the ingots were chosen so that the whole of the scandium introduced into the metal got into the aluminum solid solution during the casting process. For this purpose we overheated the melt for complete dissolution of the Al – 2% Sc master alloy and complete transfer of the scandium into the homogeneous solid solution. The ingots were cast at an elevated temperature. In addition, the ingots cast into a copper water-cooled mold were cooled intensely and uniformly even when they were withdrawn from the mold, in order to avoid discontinuous decomposition of the solid solution of scandium in aluminum, which is observed sometimes when the ingots are cooled from the casting temperature. The cooling rate in the range of the crystallization temperatures was about 100 K/sec. At such high rates of cooling alloys of the Al – Sc system crystallize in accordance with the diagram of metastable equilibrium [2]. Under the conditions of metastable equilibrium the range of existence of solid solution of scandium in aluminum widens with respect to the corresponding range in the equilibrium phase diagram. In cooling at a rate of 100 K/sec the solubility of scandium in aluminum in Al – Sc alloys attains 0.7% [3 – 4].

Basing ourselves on this reasoning we chose rapid crystallization for obtaining a material with a structure of supersaturated solid solution of scandium in aluminum.

According to the results of the measurement of the conductivity of the ingots by the eddy current method the conductivity decreased continuously from 35.5 to 27.6 MS/m upon growth in the content of scandium from 0 to 0.55%. At the same time, not the whole of the scandium introduced into the blend entered the solid solution. A part of the scandium (much lower than that determined in the solid solution) precipitated during the crystallization in the form of particles of an equilibrium $\text{Al}_3(\text{Sc}, \text{Ti})$ phase, which can be inferred from the decrease in the size of the cast grains upon growth in the scandium content in the alloy. The mean grain size in the ingots of the alloys with 0, 0.14, 0.23, 0.35, 0.40 and 0.55% Sc was 130, 79, 88, 75, 80 and 44 μm , respectively. This law of reduction of the size of cast grains in the Al – Sc alloys upon growth in the content of scandium differs from that detected in [4], which seems to be more correct in our opinion. This may be explained by the fact that all our alloys contained an admixture of titanium (0.06%), and this changed the effect of the scandium content on the size of the cast grains.

Ingots with different scandium content were used as an initial material for studying the kinetics of the decomposition of the solid solution of scandium in aluminum. The kinetics of the decomposition of the solid solution was studied by

plotting *C*-curves. We treated the ingots mechanically to prepare specimens 4 × 40 × 40 mm in size for measuring the conductivity. The treatment consisted of isothermal annealing at 250 – 55°C at a step of 50°C for different times and water cooling. One-hour isothermal holds were conducted in a melt of Pb – Bi. Longer holds were conducted in an electric furnace with air circulation. After annealing the specimens by different modes we measured their conductivity making at least five measurements for each specimen.

We averaged the results obtained and plotted the curves characterizing the variation of the conductivity of Al – Sc ingots with different scandium contents and after holding them for different times at 250, 300, 350, 400, 450, 500 and 550°C. These plots were used to obtain the *C*-curves of the decomposition of the solid solution of scandium in aluminum. Zero decomposition was assumed to correspond to the conductivity of the cast and not annealed ingots with different scandium contents under the assumption that the whole of the scandium was concentrated in the supersaturated solid solution. 100% decomposition was assumed to correspond to the conductivity of 35.5 MS/m in an ingot without scandium. It is clear that the assumption is conventional, because the conductivity of the studied Al – Sc ingots could not reach the conductivity of aluminum due to the presence of residual scandium in the solid solution whatever the annealing hold. We plotted the *C*-curves corresponding to 5, 10, 20, 40, 60 and 80% decomposition of the solid solution of scandium in aluminum under the assumption that the value of the conductivity was determined by the concentration of the solid solution of scandium in aluminum and these quantities obeyed a feedback.

RESULTS AND DISCUSSION

Figure 1 presents the curves characterizing the variation of the conductivity of Al – Sc ingots with different contents of scandium with the duration of isothermal holds at different temperatures. The conductivity increases with growth in the time of the hold. The value of maximum increase in the conductivity depends on the content of scandium in the Al – Sc alloy. In the alloys with 0.14, 0.23, 0.35, 0.40 and 0.55% Sc the conductivity is 2.5, 3.5, 4.5, 6.0 and 8.0 MS/m respectively. The behavior of the curves shows that on the whole the stability of the solid solution of scandium in aluminum is low; the rate of the decomposition of the solid solution increases and the duration of the incubation period decreases with growth in the scandium content. For a more detailed analysis of the influence of the concentration of the solid solution of scandium in aluminum on the kinetics of the decomposition of the solid solution we plotted *C*-curves (Fig. 2).

Analysis of the *C*-curves shows the following:

1. As the scandium content in the Al – Sc alloys increases, the *C*-curves shift toward shorter holds over the time axis. The incubation period decreases with growth in the concentration of the solid solution of scandium in aluminum.

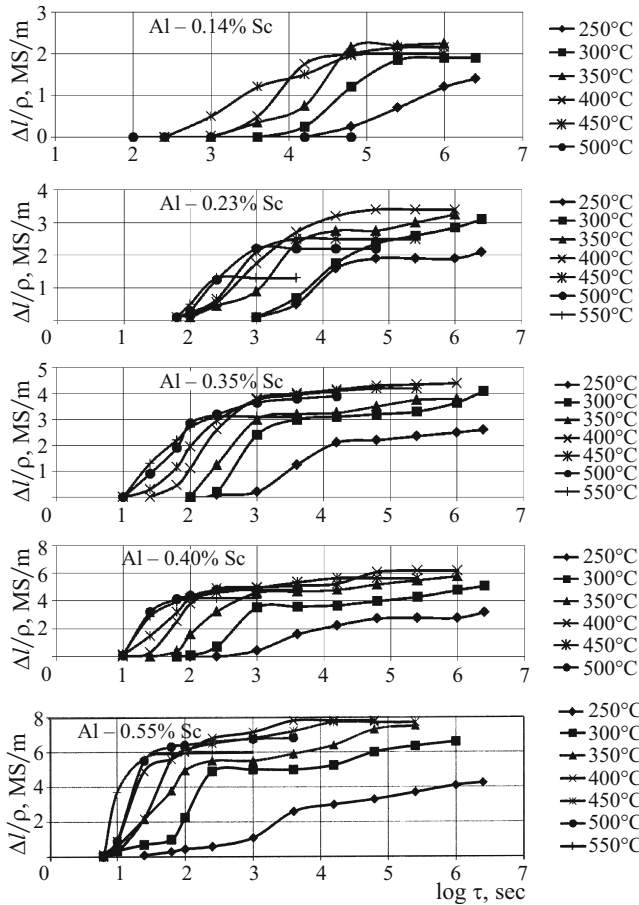


Fig. 1. Electrical conductivity of ingots from Al – Sc alloys with different scandium contents as a function of the duration of the hold at different temperatures.

Figure 3 presents the time preceding the 5, 10, 40 and 60% decomposition of the solid solution of scandium in aluminum at 400°C as a function of the scandium content in the alloy. For example, when the scandium content is increased from 0.14 to 0.55% the time to the 10% decomposition is reduced from 38 min to 24 sec. The time to the 60% decomposition decreases from 2.8 h to 1 min (curve 4 in Fig. 3). The rate of the decomposition decreases in accord with the time of the decomposition. For example, in the alloy with 0.14% Sc the time of the decomposition at 400°C from 10 to 80% is 4.2 h, while in the alloy with 0.55% Sc this time is 40 sec. If we represent the rate of the decomposition in “reciprocal” seconds, the rate of the decomposition in the Al – 0.14% Sc alloy will be $6 \times 10^{-5} \text{ sec}^{-1}$; in the Al – 0.55% Sc alloy it will be $2 \times 10^{-3} \text{ sec}^{-1}$. With growth in the scandium content from 0.14 to 0.55% the incubation period decreases and the rate of the decomposition increases by about two orders of magnitude.

Thus, the change in the scandium content and the corresponding change in the supersaturation of the solid solution of the Al – Sc alloys, which is the driving force of its decomposition, is responsible for a considerable change in the ki-

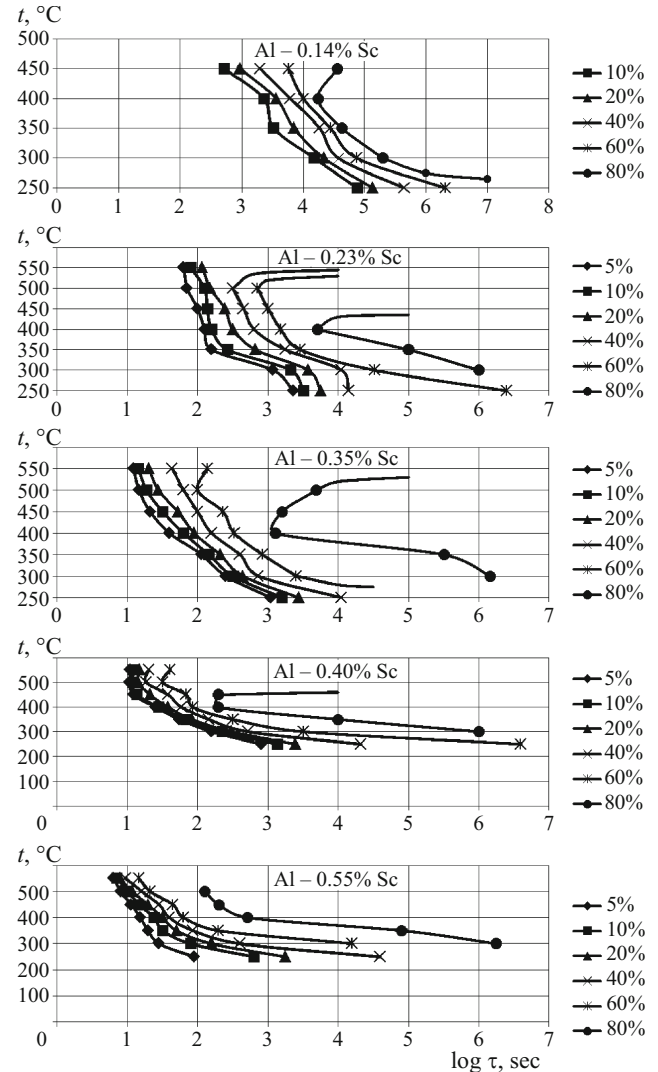


Fig. 2. C-curves of isothermal decomposition of supersaturated solid solution of scandium in aluminum in ingots from Al – Sc alloys with different content of scandium.

netics of the decomposition. This should be taken into account when we choose the temperature and time parameters for processing ingots into deformed semiproducts, and especially when we choose the parameters of the longest high-temperature homogenization of ingots from commercial alloys with different scandium content that may fluctuate in commercial alloys from 0.03 to 0.25% depending on the grade of the alloy.

2. If we estimate the rate of decomposition of the solid solution of scandium in aluminum in comparison with the corresponding rates for solid solutions of other transition alloys in aluminum, for example, of manganese, zirconium, or chromium, the former will be considerably higher, as it has been noted in [1]. For example, if we compare the kinetics of the decomposition of the solid solution in ingots of ‘Al – transition metal’ binary alloys with 0.40% Sc and 0.60% Mn, the duration of isothermal holds at 450°C until 5% decompo-

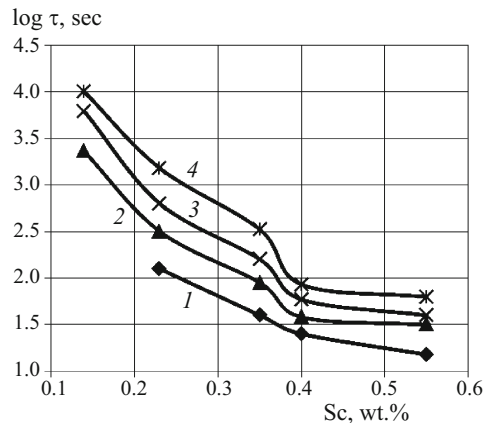


Fig. 3. Time before decomposition of the solid solution of scandium in aluminum ($\log \tau$, sec) at 400°C in Al – Sc alloys as a function of the content of scandium: 1) 5% decomposition; 2) 10%; 3) 40%; 4) 60%.

sition will be 10 sec for alloy Al – 0.40% Sc and 4 h for alloy Al – 0.6% Mn, whereas the time to the 20% decomposition will be 20 sec and 62 h, respectively. The rate of the decomposition in this time range is 10^{-1} sec^{-1} and $3 \times 10^{-7} \text{ sec}^{-1}$, respectively.

The incubation period of the 5% decomposition in ingots of alloy Al – 0.3% Zr at 450°C is 35 h.

Thus, the solid solution of scandium in aluminum is quite unsteady. We have discussed the causes of its enhanced susceptibility to decomposition earlier in [1]. The main causes are the easiness of nucleation of the Al_3Sc phase in the aluminum matrix due to the size and structural similarity of their crystal lattices and the comparatively high diffusivity. Due to the likeness of the crystal lattices the particles are precipitated in the form of an equilibrium Al_3Sc phase fully coherent to the aluminum matrix. The surface energy of such a particle is low and amounts to 0.010 J/m^2 [5]. The activation energy in the stage of nucleation and growth of Al_3Sc particles is 80 kJ/mole, which is much lower than the activation energy of the diffusion in aluminum of such transition metals as Ti ($Q = 240 \text{ kJ/mole}$) or Zr ($Q = 260 \text{ kJ/mole}$) [5]. Due to the easiness of the nucleation of particles of Al_3Sc in the aluminum matrix, the number of the simultaneously precipitated particles is great, their distribution density in unit volume of the aluminum matrix is high, and the size of the particles in the initial stage of the decomposition is several nanometers. The process of coagulation starts almost simultaneously (with a short delay) with the process of precipitation of the particles. The fine particles of Al_3Sc dissolve, scandium atoms transfer to the solid solution, diffuse over the aluminum matrix to coarser particles, and precipitate on their surface. The process goes on continuously virtually from the very start of the decomposition. This can be inferred from the curves illustrating the variation of the mean size of the particles of phase Al_3Sc , which grow right from the moment of their determination (Fig. 4).

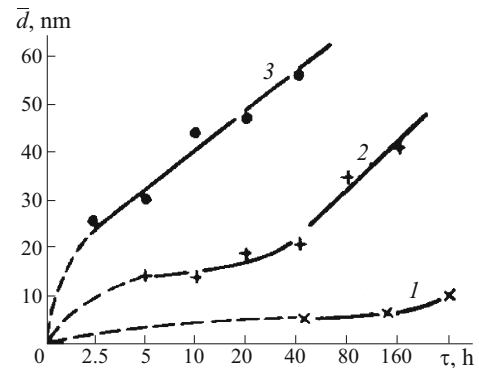


Fig. 4. Variation of the mean size of particles of the Al_3Sc phase during aging of alloy Al – 0.18% Sc at a temperature of 300°C (1), 400°C (2) and 450°C (3).

Coherent particles grow in accordance with the Lifshits – Slezov theory, when their growth is controlled by the processes occurring on the interphase separating the particle and the matrix [5]. At the same time, in [5] the solid solution of scandium in aluminum was obtained by quenching the specimens from a high temperature, when the solid solution contained quenching vacancies together with scandium atoms. Undoubtedly, the presence of the quenching vacancies affected the kinetics of the decomposition, especially its initial stages.

The process of growth of particles is violent due to extensive and intensive factors. The number of such particles is great, their density is high, and the total area of the interphase separating and simultaneously providing interaction of the particles and of the aluminum matrix is large [6]. This factor promotes “widening” and intensification of the diffusion flow connected with the decomposition of the solid solution of scandium in aluminum. In addition, since the density of the Al_3Sc particles is high and the mean distance between them is short, the mean free path of scandium atoms from a fine particle to a coarse one is short too.

It should also be taken into account that the diffusion of scandium atoms develops in the aluminum matrix with higher intensity than the diffusion of atoms of other transition metals. For example, the diffusivity of scandium in aluminum at 500°C is $10^{-11} \text{ cm}^2/\text{sec}$,² that of manganese is $10^{-12} \text{ cm}^2/\text{sec}$, and that of zirconium is $5 \times 10^{-14} \text{ cm}^2/\text{sec}$ [7]. This factor contributes into acceleration of the diffusion flow.

The mentioned factors intensify the diffusion flow of atoms connected with decomposition of the solid solution of scandium in aluminum and lower the mean length of this flow. In this connection, the process of the decomposition including the coagulation of particles of Al_3Sc develops at a high rate. The rate of the decomposition of the solid solution of scandium in aluminum estimated in terms of the decrease

² The results of the generalization published data performed by L. B. Ber are published with his permission.

in the concentration of the solid solution passes through a maximum. At the start of the process the dominant process is nucleation of particles of Al_3Sc connected with the ascending diffusion and with the formation of scandium-enriched nanovolumes in the aluminum matrix.

After the formation Al_3Sc particles the process of their coagulation starts virtually immediately. Fine particles dissolve and precipitate simultaneously, and coarse particles grow continuously due to precipitation of scandium atoms on their surface. The process of coagulation is steady for a long period. Even after the establishment of equilibrium concentration in the solid solution of scandium in aluminum at some specific temperature the coagulation process will continue.

The stage of coagulation is determinable when we analyze the curves describing the growth in the conductivity as a function of the duration of isothermal hold at 250 and 300°C. Let us consider, for example, the curve in Fig. 1 for alloy Al – 0.35% Sc at a temperature of 250°C. Up to a hold of 10^3 sec we observe an incubation period; the next stage is precipitation and simultaneous coagulation of Al_3Sc particles. At a temperature of 250°C and a hold for $10^{4.2}$ sec the concentration of the solid solution of scandium in aluminum attains equilibrium, and the precipitation of particles finishes. Then follows the processes of coagulation and growth of the particles of Al_2Sc , the driving force of which is decrease in the area of the interphase. This period continues for from $10^{4.2}$ to $10^{6.4}$ sec. It seems that it will continue until the particles lose their coherence, after which the kinetics of the coagulation process should change.

CONCLUSIONS

1. Variation of electrical conductivity has been used to plot *C*-curves of isothermal decomposition of the solid solu-

tion of scandium in aluminum in binary Al – Sc alloys, where the actual scandium content was varied from 0.14 to 0.55%.

2. Growth in the scandium content accelerated markedly the decomposition of the solid solution of scandium in aluminum. For example, when the scandium content was increased from 0.14% to 0.55%, the rate of the decomposition fell by two orders of magnitude, and the incubation period shortened by two-three orders of magnitude.

3. On the whole, the solid solution of scandium in aluminum decomposes 3 – 4 orders of magnitude faster than the solid solutions of other transition metals in aluminum, for example, of manganese or zirconium. The causes of accelerated decomposition of the solid solution of scandium in aluminum have been discussed.

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