OXIDATION OF ALUMINUM ALLOYS IN THE PROCESSING CONDITION

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Abstract: *An important characteristic of the nano-microcrystalline ribbons based on Al-Si alloys, that we have studied, is their propensity for oxidation at high temperatures. The amount of oxides formed during the preparation or consolidation of rapidly solidified alloys, are protected the melts from the air. The oxide layer hinders contact between the microcrystalline ribbons during hot extrusion and deteriorates the mechanical properties of the obtained blanks. The hot extrusion process is carried out at temperatures above T = 400 °C. The heating of the ribbons during extrusion creates preconditions for further oxidation of the metal and increase of the oxide layer over time. Knowledge of the oxidation process allows to minimize the impact of the oxide layer on the structure and properties of the extruded blanks. The high wear and tear strength of Al-Si alloys makes them an important material for use in the automotive and aerospace industries for making various details such as pistons, cylinder blocks, bushings, bearings.*

The study of the oxide layer formation and its properties have been made on the basis of the formal Nikitine kinetics.

ОКИСЛЯВАНЕ НА АЛУМИНИЕВИ СПЛАВИ В УСЛОВИЯТА НА ПРЕРАБОТКА

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Резюме: *Важна характеристика на изследваните от нас нано-микрокристални ленти на основата Al-Si сплави е склонността им към окисление при високи температури. Количеството оксиди, образували се по време на получаване или консолидиране на бързо затвърделите сплави предпазват добре стопислките от въздуха. Оксидният слой пречи за установяване на контакт между микрокристалните ленти при екструзията на горещо и влошава механичните свойства на получените масивни заготовки. Процесът на гореща екструзия се провежда при температури над T = 400 °C. Нагряването на лентите по време на екструзията създава предпоставки за допълнително окисление на метала и нарастване на оксидния слой във времето. Познаването на окислителния процес позволява да се вземат мерки за минимизиране на вредното влияние на оксидният слой върху структурата и свойствата на екструдираните заготовки.*

Кинетиката на нарастване на оксидния слой е изследвана убедително в статията. За целта се използва формалния подход на Никитин.

1. Introduction

Nano-microcrystalline alloys (ribbons) are substantially different from the massive alloys as shown in Fig. 1. In the case of the production of ribbons, the application of elevated temperatures is necessary, for consolidation the ribbons to bulk samples. The study of the mechanism of alloy interaction with the air in the conditions of hot extrusion is necessary. The studying of interaction of alloys with air is important for processing the waste alloys as well.

Fig. 1. Nano-micro crystalline ribbon

This paper explores the kinetics of oxide layer formation on nano-microcrystalline ribbons at temperatures of hot melt extrusion. For the data processing, the formal Nikitin kinetics method was applied for working experimental weight gain time curves [1, 2]. The influence of the alloying elements on the oxidation velocity and some properties of the surface oxide coating is shown. The results are compared with these, received with in [2], where the authors studied bulk samples.

2. Experimental procedure

Nano micro crystalline alloys are obtained in a laboratory plant using the Planer Flow Casting method (PFC) [3, 4, 5]. The melt solidifies at a rate of 10^{5-6} K/s. In Fig. 1, such a ribbon of base alloy 2 has been shown.

Under these conditions a two-zone metal ribbons is obtained. The two zones are on both sides of the ribbon: WS (facing the wheel site), where the particles are in nanoscale and AS (facing the air site), where the particles grow to the microscale. Nevertheless the particle size of the whole ribbons differ strongly from particle size of bulk alloys.

The increase in the specific weight W of the specimens during the experiment is monitored using SETERAM thermo scales.

A least-squares method of calculations was conducted to find the most expected curves by PC. A standard χ^2 (chi squared) test was used to test the quality of the fitting.

The chemical composition of the studied alloys is shown in Table 1.

Table 1. Chemical composition of the ribbons in wt. %

Ribbon	Si	Fe	Mg	Al
1	11.75	0.32	0.61	87.32
2	11.50	0.25	0.27	87.98
3	12.10	2.00	0.20	85.70

Figure 2 shows experimental curve data in the study of the resistance of studied ribbons to high temperature oxidation at T = 550 °C. These results are obtained in [4]. Apparently, the oxide coating on the ribbons increases parabolically over time, Fig. 2. We tested whether we could apply Nikitin's approach to obtaining information from the growth of the oxide coating [1]:

(1) $$W_i = a.t$$

By comparing the oxidation results of the different samples, it is possible to conclude about the effect of the composition of the nano-microcrystalline ribbons on the oxidation process. The obtained alloys contain different alloying elements as shown in Table.1.

Demonstration of the oxidation mechanism is one of the tasks of this study, which necessitates finding a method for calculating the experimental results.

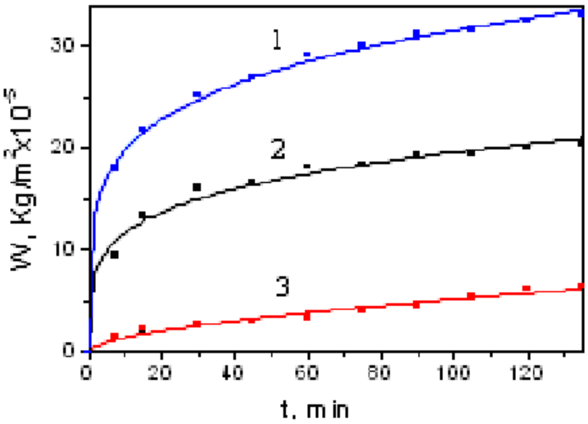

Fig. 2. Increase of the oxide layer on the examined microcrystalline ribbons (weight gain – time curves): 1, 2, 3 at T = 550 °C for 120 min

The following samples are considered:

1 - ribbon with an increased Mg content;

2 - ribbon basic;

3 - ribbon with an increased Fe content.

It can be seen from Fig. 2 that the low iron ribbons (1 and 2) have a higher tendency to oxidation at elevated temperatures. The increase in the oxide layer of nano-microcrystalline ribbons in the hot extrusion process at T = 450 – 480 °C is negligible and the kinetics studies are carried out at 550 °C.

To clarify the mechanism of oxidation of nano-microcrystalline alloys, the formal kinetics of Nikitin were used. By variation of the exponent n in the equation (1), we found the exact value of n at which two parameters curves fit best the experimental points from Fig. 2, i.e. at which square functional (2) has a minimum value [4].

3. Mechanism of the growth of the oxide layer.

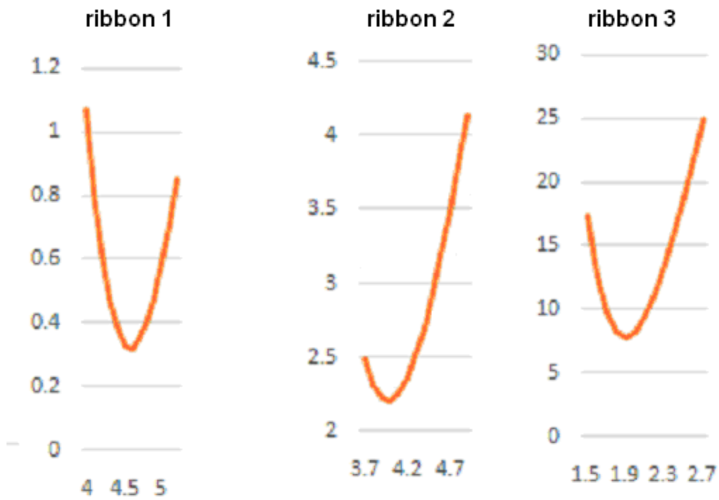

Fig. 3. Dependence of χ^2 on determine n

According to Nikitin theory, the increase in the oxide coating W_i relative to time t follows the equation (2), where a is a parabolic constituent. To determine n, calculate χ^2 of formula (2):

$$\chi^2 = \sum_{i=1}^{10} \left(\frac{Wi(t) - Wi(\exp)}{0.1 Wi(\exp)} \right)^2, \quad (2)$$

where W_i are the experimental points.

To calculate the value of χ^2 for specific values n, follow the sequence of actions:

1. We replace $W_i(t)$ with $\sqrt[n]{a.t}$ thus, revealing the brackets, we get a square function which has the form:

(3) $$(\sqrt[n]{a})^2 = (100\sum_{i=1}^{10}\frac{\sqrt[\frac{n}{2}]{t(i)}}{Wi(\exp)^2}) - (\sqrt[n]{a})(200\sum_{i=1}^{10}\frac{\sqrt[n]{t(i)}}{Wi(\exp)}) + 1000$$

2. To have the smallest value, its first derivative value is zero, which is performed for:

(4) $$\left(\sqrt[n]{a}\right) = (100\sum_{i=1}^{10}\frac{\sqrt[n]{t(i)}}{Wi(\exp)}) / (100\sum_{i=1}^{10}\frac{\sqrt[\frac{n}{2}]{t(i)}}{Wi(\exp)^2},$$

where we find the constant α and replacing the value in formula (3).

3. We find the corresponding value for χ^2 for a specific n. We compute the values for several different ns and get the minimum of them that corresponds to the desired metric in the initial equation of Nikitin.

Table 2. Results of oxidation kinetics study

Ribbon	Exponent n
1	4.7
2	4.1
3	2.0

With the highest value of the exponent n (4.7) (Table 2), therefore the highest oxidation tendency has ribbon 1 (Mg content = 0.61 wt. % in it). As can also be seen in Fig. 1, that alloy 3 has the thickest oxide coating, which emphasizes the effect of Mg on increasing the tendency of aluminium alloys to oxidize.

The exponent n for ribbon 3 is exact 2.0. The result of the oxidation process is strong oxide coating, which protects alloys from next oxidation. The protective proprieties of oxide layer are nearly the same as protective properties of pure aluminium. The detrimental elements Fe become useful because of PFC method for receive of ribbons.

Conclusions

1. The results of a kinetic study of the oxidation process show that some alloying elements have a significant influence on the oxidation tendency of Al-Si alloys.
2. The results of weight gain-time studies at 550 °C fit the parabolic low for nano-microcrystalline Al-Si alloys with Fe concentration about 2 wt. %. Thus Fe, because of method of very fast solidification, become useful addition as alloys show decreased oxidation tendency with thin and strong oxide skin and n is exact equal to 2. This is a prerequisite for the preparation of massive samples of good density in subsequent treatment of the waste from the production of these alloys.
3. The alloys doped with Mg show increased oxidation tendency compared to other two studied alloys. The exponent n >> 2. Secondary processing of these alloys is very volatile, because oxidative processes will continue and create opportunities for increasing number of defects.
4. Formal kinetics makes it possible with comparatively available means to predict the properties of samples obtained by hot extrusion from fast-solidified aluminium alloys.

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