ON THE QUESTION OF MODIFYING ALUMINUM WITH TRANSITION METALS

![Fig. 1](image)

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Fig. 1

Figure 1: Fig. 1

Abstract

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PHYSICS

L. K. LAMIKHOV, G. V. SAMSONOV

ON THE QUESTION OF MODIFYING ALUMINUM WITH TRANSITION METALS

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Additions of certain transition metals are widely used for refining the grain of aluminum alloys. M. Eborall (1) invokes the theory of the concentration gradient to explain the modifying action of transition metals. In the works of M. V. Mal' tsev (2–4), ideas are developed about modification as a process associated with the formation of particles of refractory intermetallic compounds, serving as nuclei of crystallization centers. He believes that the effectiveness of a modifier is determined by the closeness of the lattice parameters of the aluminumide formed and of aluminum, the discrepancy between which should not exceed 10-12%. Without denying the possibility, in some cases, of explaining grain refinement through the formation of aluminumides, A. Tsibulya (5) explains the modifying action of transition metals by their ability to form carbides; moreover, carbides of Ti, Zr, V, Nb, Ta, Mo, W, possessing simple types of crystal lattices, can serve as nuclei for the formation of crystallization centers if the difference in interatomic distances in the carbide and aluminum lattices does not exceed 16%. On the contrary, carbides of Mn, Fe, Co, Ni, Cr, which have complex crystalline structures, do not possess the ability to modify.

Fig. 1. Dependence of the effectiveness of the modifying action on aluminum of transition metals on the degree of acceptor ability of their *d*-electron shells

In work (6), the modifying ability of transition metals is explained by the presence of a peritectic in the aluminum—transition metal system.

Let us note the following shortcomings of the existing theories.

1. Modern ideas about the structure of liquid metals and alloys are not brought in to explain the modification process.
2. Theories that explain the process of modification of aluminum alloys by the presence of carbide particles (5) or a peritectic reaction (6) are based on dividing all transition metals into two large groups: modifying metals and nonmodifying metals. However, from experimental data it is known

> that additions to pure aluminum of any transition metals (including "nonmodifiers") lead to grain refinement. In essence, all transition metals possess a greater or lesser modifying ability, in connection with which it is impossible to draw a sharp boundary between modifiers and nonmodifiers. Only in the works of M. V. Mal' tsev (2–4) is an attempt made to uncover the reasons for the differing effectiveness of one modifier in comparison with another. However, the explanation of this fact by the closeness of the lattice parameters of the "substrate" and the crystallizing ···

phase contradicts a number of experimental data. In particular, V. I. Danilov (7) pointed out that the action of an "activated" impurity is not limited to the requirements of structural and size matching.

In all works devoted to this question, no attempts are made to establish any correspondences between the electronic structure of the modifier and that of the metal being modified, although it may be assumed that such a correspondence is primary and determines all other factors.

The modifying action of transition metals—whether it reduces to the formation of nuclei in the form of carbides or aluminides, or to a concentration gradient —must ultimately be determined by the activity, the reactivity of transition metals, expressed by criteria of the degree of incompletion of the *d*-electron shells of their atoms.

Table 1

Effect of transition metals on the grain refinement of aluminum AB000

Element	n	$1/Nn$	Maximum number of grains per 1 cm^2	Element	n	$1/Nn$	Maximum number of grains per 1 cm^2
VI period				V period			
Sc	1	0.333	1090	Zr	2	0.125	840
Ti	2	0.167	900	Nb	4	0.0625	121
V	3	0.111	400	Mo	5	0.05	121
Cr	5	0.067	36	VI period			
Mn	5	0.067	49	Ta	3	0.067	625
Fe	6	0.055	64	W	4	0.050	256
Co	7	0.047	25	Re	5	0.040	81
Ni	8	0.041	16				

As such a criterion in the present work we used the quantity $1/Nn$ (N is the principal quantum number of the incomplete d-shell, n is the number of electrons in this shell) ([8]), which has been called the acceptor or scattering ability of the d-electron shell of the transition-metal atom.

We carried out experiments on the modification of aluminum AB000 with fourteen transition metals of periods 4, 5, and 6. The experimental procedure did not differ in principle from the methods described in works ([1,6]). The modifying effect from introducing one or another addition was quantitatively expressed by the number of grains per 1 cm^2 of the polished-section surface. The experimental results are given in Table 1. The influence of scandium and rhenium additions on the size of the macrograin of aluminum was investigated, as far as we know, for the first time in the present work.

From the data of Table 1 it is evident that the elements that begin periods and have the greatest deficiency of the d-level possess the greatest modifying ability. For example, scandium is the most effective modifier, and as the d-level is filled from scandium to nickel, the modifying ability of the metal decreases. The same regularity is also observed for elements of other periods. It is interesting that some deviations from these dependences are observed for chromium and manganese, which have fairly stable electronic configurations d^5s^1 and d^5s^2, with a corresponding lowering of acceptor ability in comparison with that following from the criterion $1/Nn$.

In Fig. 1, in semilogarithmic coordinates, the dependence of the modifying action of transition metals on the degree of acceptor ability of their d-electron shells is presented.

The data obtained in the present work agree well with previous observations made on the basis of analysis of experimental results of other investigators ([9]).

Obviously, the considerations set forth can be extended not only to aluminum alloys, but also to copper alloys, with respect to which titanium and zirconium are likewise effective grain refiners ([10]).

The mechanism of grain refinement may be associated with the presence, in the melt of aluminum modified by strongly acceptor transition metals, of quasi-molecular groupings of atoms (more precisely, atomic islands) of the transition metal and aluminum, similar, for example, to the groupings of iron and silicon atoms in melts of iron-silicon alloys ([11]); the capacity for strong interaction of such groupings with one another, also established in the work cited, explains well the phenomenon of "overmodification" (grain coarsening upon passing through a certain critical concentration of the modifier).

According to the data of work ([5]), lanthanum and cerium do not refine the grain of aluminum. The author of that work believes that lanthanum and cerium form dicarbides of the type MeC_2, the particles of which cannot serve as nuclei for the formation of crystallization centers because of the great difference between the lattice parameters of these compounds and aluminum.

From the standpoint of electronic structure, the absence of modifying properties in lanthanum and cerium can be explained as follows. Lanthanum and cerium belong to the f-transition metals with deeply incomplete $4f$-shells, which cannot directly participate in chemical bonding, but can ensure the appearance of d-states through $4f^n \to 4f^{n-1}5d$-transitions. Although for lanthanum and cerium the possibility of such transitions, determined by the small number of possible terms (Fig. 2) ([12]), is sufficiently great, this determines not the acceptor, but the donor capacity of these elements, expressed, for example, by the low work function in thermionic emission of some of their compounds ([13]), which makes their modifying action unlikely; this action, as was shown above, is associated with the capacity of the transition metal to accept electrons of aluminum. It is more probable that the second subgroup of rare-earth elements (from gadolinium to lutetium) possesses modifying properties, taking into account the strong shielding of the $5d$-orbitals from the nuclear field by the $4f$-shell, which is very saturated with electrons.

Fig. 2. Number of possible terms for the f-electrons of lanthanide atoms

Thus, one of the principal factors determining the modifying capacity of transition metals is the number and energy state of the electrons in the incomplete shells of the isolated atoms of these metals, which should serve as the starting point for constructing a rational theory of the modification of aluminum and its alloys.

Chemical-Metallurgical Institute
Siberian Branch of the Academy of Sciences of the USSR

Institute of Metal Ceramics and Special Alloys
Academy of Sciences of the Ukrainian SSR

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CITED LITERATURE

1. M. Eborall, *J. Inst. Metals*, **76**, 295 (1949).

2. M. V. Mal' tsev, *Transactions of the Moscow Institute of Non-Ferrous Metals and Gold named after M. Kalinin*, No. 25, 331 (1955).

3. M. V. Mal' tsev, in: *Collection: Light Alloys*, No. 1, Publishing House of the Academy of Sciences of the USSR, 1958, p. 273.

4. M. V. Mal' tsev, *Modification of the Structure of Metals and Alloys*, Author' s abstract of doctoral dissertation, Moscow, 1954.

5. A. Cibula, *J. Inst. Metals*, **76**, 321 (1949).

6. F. Crossley, L. Mondolfo, *J. Metals*, **3**, 1143 (1951).
7. V. I. Danilov, *Problems of Metallurgy and Physics of Metals*, Moscow, 1949, p. 7.
8. G. V. Samsonov, *DAN*, **93**, 689 (1953).
9. L. K. Lamikhov, G. V. Samsonov, *Izv. AN SSSR, OTN, series Metallurgy and Mining*, No. 2 (1963).
10. A. Cibula, *J. Inst. Metals*, **82**, 513 (1954).
11. P. V. Gel' d, M. S. Petrushevskii, *Izv. AN SSSR, OTN, series Metallurgy and Fuel*, No. 3, 160 (1961).
12. G. V. Samsonov, V. S. Neshpor, *DAN*, **122**, 1021 (1958).
13. G. V. Samsonov, Yu. B. Paderno, *Borides of Rare-Earth Metals*, Kiev, 1961.

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