INTERMETALLIC COMPOUNDS OF RARE-EARTH METALS WITH ALUMINUM AND SOME OF THEIR PROPERTIES

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The large number of engineering fields in which the rare-earth elements are widely employed testifies to the valuable physicochemical properties of these metals and their compounds.

In the nonferrous and ferrous metallurgy, the rare-earth metals are used as inoculating and alloying additions to improve the properties of alloy. Generally, they are employed in the form of master alloys consisting of natural, inseparable mixtures of two or more rare-earth metals (mischmetals). The mechanism of inoculation and alloying of industrial alloys with the rare-earth metals has so far received little study; particularly little information is available on the influence of individual rare-earth element. Results of investigations indicate that small additions of the rare-earth metals (0.25-0.40%) to aluminum alloys raise the mechanical properties of the latter by 20-30% and, at the same time, increase their elongation by 50-100%. At high rare-earth metal contents, aluminum alloys acquire heat-resisting properties. An example is the cast heat-resisting aluminum-cerium alloy ATsR-1.

Further investigation into the influence of the rare-earth metals on various alloys will necessitate the production of master alloys of the individual rare-earth metals with aluminum, magnesium, and other metals on an industrial scale. This will substantially lower the cost of these materials and widen the scope of investigation and application of the rare-earth metals in metallurgy. Particularly important is the problem of the development of various alloys and chemical compounds based on the rare-earth metals, which will be used in future as materials with specific physicochemical properties, such as heat-resisting alloys, catalysts, semiconductors, ferroelectric materials, etc.

The rare-earth elements belong to the class of d-transition metals. A characteristic feature of these metals is the incompleteness of the deep 4f level of electrons in the atom, which are capable of participating in chemical bonds. As was demonstrated in [1], this is due to the fact that atoms of the rare-earth metals (except gadolinium, terbium, and lutecium) in the normal state have no 5d electrons, although twice ionized atoms are characterized by $4f^N \rightarrow 4f^{N-1}5d$ transitions. Consequently, when f-d transition are present and the energies of the 4f and 5d states are similar, 5d electrons with s-d bonds may form.

In recent investigations, many authors employed high-purity metals and obtained more accurate data on the phase diagrams of the rare-earth metals with aluminum. Taking into account these data, the phase diagrams presented in Fig. 1 were examined in the present investigation. All these diagrams are of the eutectic type, and contain between 4 and 5 intermetallic compounds corresponding to the formulas $Me_3Al$, $MeAl$, $MeAl_3$, $MeAl_4$, and $Me_3Al_2$. In addition, there are data on chemical compounds found in practically all systems of the rare-earth metals with aluminum, even though the phase diagrams of these systems have not yet been constructed. The crystalline structures of some compounds are yet to be determined. There is a controversy as to whether compounds of the $Me_2Al_2$ composition exist in the systems of aluminum with the cerium subgroup metals (La-Eu).

All known phase diagrams of aluminum with the rare-earth metals lanthanum, cerium, praseodymium, neodymium, and their analogs, yttrium and scandium, are of the same type, and closely resemble the phase diagram of aluminum with calcium. The rare-earth metal group lies in the close vicinity of the alkaline-earth metal group, their compounds with aluminum have similar chemical properties, and their atomic radii are similar ($r_{Ca} = 1.97$ and $r_{La} = 1.87$ Å). As in the case of the rare-earth metals, the ionization potentials of the alkaline-earth metals are very close to that of aluminum. This permits the development of s-p bonding, while the presence of a d level which is optically free from electrons ($d^0s^2$ electronic configuration) in the alkaline-earth metals opens up the possibility of development of s-p-d bonding.

*The division of the rare-earth metals into two subgroups is based on their electronic structure and melting points.

An examination of the systems of aluminum with the metals of subgroup IIa (Ca, Sr, Ba) on one hand and with the metals of subgroups IVa (Ti, Zr, Hf) and Va (V, Nb, Ta) on the other shows that, in the former case, the aluminum-rich compounds always have the formula MeAl$_4$, whereas the aluminum-rich intermetallic phase in the other two subgroups has the composition MeAl$_2$. The rare-earth metal group is located between them, and as it were inherits the features of the first of the metal subgroups considered. This manifests itself in the presence in the cerium metal subgroup of an aluminum-rich compound with the composition MeAl$_4$ in the yttrium subgroup of the rare-earth metals, the aluminum content of the compound decreases, giving the composition MeAl$_3$. The replacement of MeAl$_4$ by MeAl$_3$ is linked with a change in the electronic structure of atoms of these metals, manifesting itself in increased filling of the 4f shell (more than 7 electrons), since in the interatomic bonds of a crystal of the resulting compound participate not only the outer s electrons, but also more strongly bonded electrons of the inner energy levels.

The presence of a large number of electrons in the 4f shell results in an increase of the positive charge of the nucleus in order to secure electrical neutrality of the atom. On the other hand, the electrons on the 4f shell do not fully shield one another, or neutralize the influence of the outer electrons, and the increased nucleus charge subjects the electrons of the 4f shell and the external shells to the influence of a larger positive charge compared with the electrons of elements with smaller atomic numbers. In other words, as the effective nucleus charge increases, the electrons of the 4f shell and all valence electrons are drawn closer to the nucleus and held more firmly, resulting in a decrease in the radii of these electron shells. This phenomenon is known as the lanthanide contraction. The increase in the stability of electronic configurations with increasing atomic number of elements is clearly illustrated by the change in the chemical composition of intermetallic compounds from lanthanum to lutecium.

For the compounds MeAl$_4$, the bond between the individual atomic layers is less pronounced than, for example, for the analogous compounds of calcium and, particularly, strontium and barium, since it cannot be presumed that the lanthanum or cerium atoms in the elementary cell of the crystalline structure of these compounds are in contact with one another ($a$ < $2r_{La, Ce}$) or are bonded together by a dense electron cloud. In fact, stability in these intermetallic compounds is greater than, for example, in SrAl$_4$. It appears that, in the MeAl$_4$ compounds of the rare-earth metals, a marked transition to a high-coordination lattice begins to be realized. A lanthanum or cerium atom in such compounds is surrounded by 16 aluminum particles. It is the formation of a crystalline lattice with such a high coordination number that accounts for the stability of these compounds. All compounds of the rare-earth metals with aluminum with the compositions MeAl$_4$ and MeAl$_3$ are formed as a result of peritectic reactions.

A compound with the composition MeAl$_3$ is observed in all systems from scandium to lutecium. It crystallizes out of the melt, and its melting point is higher (>1400°C) than those of compounds of other compositions.

It is probable that, for each rare-earth metal, there is also a compound of the composition MeAl. So far, such compounds have not been established for the systems of yttrium, lanthanum, cerium, praseodymium, neodymium, gadolinium, and dysprosium. They form as a result of peritectic reactions.