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# I. I. Kornilov

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**Abstract**

**Full Text**

**I. I. Kornilov**

## **Metallochemical Properties of Niobium**

*(Presented by Academician I. I. Chernyaev, 27 VI 1960)*

In one of our works (<sup>1</sup>), the metallochemical properties of the elements of the periodic system were considered. On the basis of a generalization of the results of studying the interaction of metals with one another and with metalloids, the principal types of chemical interaction were established and a classification was given for the formation among metals of continuous solid solutions, limited solid solutions, compounds with a metallic character of bonding, and compounds with ionic bonding. These questions were examined by us using the examples of iron (<sup>2</sup>), nickel (<sup>3</sup>), and titanium (<sup>4</sup>).

In connection with the study of metallic alloys based on refractory metals, it is of interest to consider the metallochemical properties of such analogous metals as niobium and tantalum, molybdenum and tungsten, and others having melting points above 2000°. In the present work the metallochemical properties of niobium will be set forth, and the elements of the periodic system will be classified according to the types of their interaction with niobium.

As the principal characteristics of the metallochemical properties of the elements we have taken: the electronic structure of the atoms, atomic radii, electronegativity, types of crystal structure, melting temperatures, and others. Niobium belongs to the elements of group V; as one of the transition-group metals, it has an unfilled outer *d*-electron shell. The atomic radius of niobium, 1.45 Å, is very close to the atomic radii of the metals neighboring it; in the series of metals according to electronegativity given in work (<sup>5</sup>), niobium occupies a middle position: about 35 metals are electropositive with respect to niobium, and 37 are electronegative; niobium has a body-centered lattice and a melting point of 2415°. The degree of similarity and difference of these metallochemical properties of niobium, arising from the close or distant position of niobium and the elements in the periodic system, determines the possible types of interaction of niobium with them or the absence of such interaction. On the basis of a generalization of the literature material on the chemical interaction of niobium with the elements of the periodic system, it is possible to classify these elements from the standpoint of their interaction with niobium.

In the general 18-row table of the elements of D. I. Mendeleev, we have placed niobium in the upper part, and all the remaining elements have been distributed among four families capable of forming with it solid solutions, metallic and ionic compounds, or incapable of any interaction. Such a table is presented in Fig. 1. In it, the first family includes only 8 metals situated close to niobium in

Fig. 1. Interaction of niobium with elements of the periodic system. Elements forming continuous solutions, limited solid solutions and compounds, ionic compounds, and noninteracting elements are indicated in the diagram.

Figure 1: Fig. 1. Interaction of niobium with elements of the periodic system. Elements forming continuous solutions, limited solid solutions and compounds, ionic compounds, and noninteracting elements are indicated in the diagram.

the periodic system and having a small difference in metallochemical properties. They are capable, on crystallization with niobium, of giving continuous solid solutions. These include: Ti, Zr (group IV), V, Ta, Pa (group V), and Mo, W, and U (group VI). Literature data <sup>(6)</sup> confirm in the main the presence of such solid solutions in these systems. It should be borne in mind that metals such as Ti, Zr, and U, owing to the presence of polymorphic modifications,

show a discontinuity in the continuity of solid solutions at low temperatures.

The second family encompasses a large group of elements capable of forming with niobium limited solid solutions and, beyond the solubility limits, a series of compounds with a metallic character of bonding. As is seen from Fig. 1, this family of elements includes both metals of groups II, III, VI, VII, VIII, and other groups, and also certain metalloids of different groups of the periodic system (B, C, Si, H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, etc.), which have a greater difference in metallochemical properties from niobium than do the metals of the first family.

The number of such elements, including the lanthanides, is only 58. To some extent, 10 elements belonging to the actinide group should be assigned to this family; then the total number of elements prone to forming

**Fig. 1.** Interaction of niobium with the elements of the periodic system. The lanthanides are marked with one asterisk, the actinides with two asterisks. **I** – elements forming continuous solutions, **II** – elements forming limited solid solutions and compounds, **III** – elements forming ionic compounds, **IV** – noninteracting elements.

limited solid solutions and metallic compounds with niobium will be only 68.

Of the total number of elements assigned to the second family, the interaction of niobium has been studied experimentally with only 27 elements. The phase diagrams of these systems show the presence in them only of limited solid solutions of niobium and the formation of a number of metallic compounds. The limiting solubility of elements in niobium decreases as the difference between the metallochemical properties of niobium and of the elements increases.

Thus, for example, the decrease in limiting solubility in niobium in the series of metals Cr, Mn, Fe, Co, and Ni follows the order of increase in their atomic number, the difference in electronegativity, and atomic radii. The tendency toward the formation of Nb compounds with metals also apparently obeys this rule.

Compounds of niobium with metalloids (B, C, Si), borides, carbides, and silicides of niobium have a metallic type of bonding.

Very limited solid solutions and compounds of niobium with N, P, As, Sb, and O (lower oxides) also possess metallic properties. The degree of decrease in the metallic properties of niobium compounds with the indicated elements increases as the difference in metallochemical

properties of niobium and these elements, which promotes the transition from metallic niobium compounds to compounds of the semiconductor type.

The third family of elements (see Fig. 1) belongs to typical metalloids, the most electronegative elements, which are not capable of forming solid solutions with niobium. In interaction with niobium they form only compounds with a covalent or ionic type of bond. Some of these compounds possess semiconductor properties. The total number of elements is 9. These include elements of VI and VII (B subgroups), where oxygen occupies an intermediate position, forming limited solid solutions with niobium and the compound NbO (possibly also Nb<sub>3</sub>O) with metallic properties.

The remaining elements—sulfur and its analogues, fluorine and its analogues—form compounds with niobium with ionic bonding; the compositions of these compounds correspond to valence relations.

Finally, the fourth family of elements comprises groups I and II (with the exception of hydrogen and beryllium) and the group of inert gases. The family of these elements does not interact at all with niobium and forms with it neither solid solutions nor compounds. The total number of these elements is only 16.

The absence of interaction of these elements with niobium is explained by very large differences in atomic radii (more than 15–16), in their melting and boiling points (elements of the alkali and alkaline-earth groups), and by inertness toward chemical reactions (all elements of the zero group).

Thus, from the point of view of the chemical interaction of niobium with the elements of the periodic system, or the absence of interaction, they may be divided into 4 families. Of these four families, the elements of the first two families are related to the metallic character of interaction. The total number of such elements is 9 and 68, altogether 77 elements. This gives grounds for considering all 77 elements as possible components for the formation of metallic alloys based on niobium. Starting from a predetermined number of elements capable of forming continuous or limited solid solutions and metallic compounds with niobium, one can calculate the concentrations of these components in simple and multicomponent niobium systems and synthesize alloy compositions with specified structure and properties.

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*Note: Figure translations are in progress. See original paper for figures.*

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