THE POSSIBILITY OF REDUCING THERMAL CONDUCTIVITY IN ALLOYS

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Reduction of thermal conductivity in nickel—titanium alloys by doping with elements having the greatest effect on phonon and electron components of thermal conductivity is considered.

Creation of new materials with specified properties, for example, specific heat, is an important problem in materials science. The most stable alloys with parameter values at the limits of the attainable range can be used as thermal conductivity references for testing measurement equipment by All-Union State Standard (GOST) 8.140-82 [1]. It is especially important to produce materials with thermal conductivity values in the range 3-7 W/(m·K) for metrological references for regular production measurement devices such as the IT-λ-400, ITS, ITEM, etc. [2]. Below we will consider the possibilities of creating such materials from alloys.

It is well known that the lowest thermal conductivity occurs in alloys the structure of which is a solid solution, with elements which dissolve in the matrix to a limited degree having a greater effect on changes in thermal conductivity than elements which freely dissolve in the matrix. Thermal conductivity is a structure-sensitive property. Thus, for example, quenching and plastic deformation, which increase the number of defects such as vacancies, dislocations, etc., decrease thermal conductivity, while annealing, which reduces defect concentration, increases thermal conductivity [3]. However, decreasing thermal conductivity of the alloy by creating a high concentration of defects is not a suitable approach in the present case, since it fails to satisfy one of the basic requirements for working standards and references, that of stability.

Of the industrial alloys, titanium—nickel ones have the lowest thermal conductivities (Tables 1 and 2).

We will consider two factors which produce an additive contribution to thermal conductivity — electron and phonon components [10-13].

The electron thermal resistance (the reciprocal of the electronic component of thermal conductivity) is given by

$$W_e = \frac{1}{\lambda_e} = W_i + W_0 + \Delta W.$$

TABLE 1. Thermal Conductivity of Titanium Alloys at 300°K

Alloy	Thermal conductivity, W/(m·K)	Defect concentration, mass%					Reference
		Al	Sn	V	Cr	Mo	
VT3-1	7,2	5,47	2,5*	—	—	—	[4]
VT6	7,6	6,0	—	4,0	—	—	[5]
VT3	7,1	6,0	—	—	2—3	—	[6]
TS5	7,5	5,5	2,5	—	—	1,5	[7]
VT14	7,4	5,4	—	1,3	—	3,4	[4]
VT15	8,0	3,0	—	—	11	8	[5]

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TABLE 2. Thermal Conductivity of Nickel Alloys at 300°K

Alloy	Thermal conductivity, W/m·°K	Defect concentration, mass%							Reference
		Fe	Cr	W	Mo	Ti	Al	The rest	
ZhS6K	8,4	2	10,5—12,5	4,5—5,5	3,5—4,5	2,5—3,0	5—6	0,15C 0,02B	[8]
KhN70VMYuT	8,0	—	14—16	—	3—5	1,0—1,4	1,7—2,2	4—6Nb	[8]
ÉP-765	8,0	—	13—16	4—6	3—5	0,9—1,4	1,7—2,3	—	[9]

In accordance with this expression a basic technique for increasing thermal resistance is increase of the impurity term. Considering that $W_0 \sim \rho_0$, and using an expression for ρ_0 from [14], we obtain

$$W_0 \sim \sqrt{nE_F Q_i(E)}.$$

It has been established that the scattering section is larger, the larger the difference in the atomic dimensions of the basic element and the impurity. The section for scattering on dissolved atoms of the transition metals is anomolously high, due to a resonant effect related to partial filling of the d shell. Thermal resistance increases greatly in metals with a high Fermi energy, especially those (the transition metals) in which the mean energy of the d shell is close to the Fermi level of the basic metal.

We will now consider the second thermal conductivity component, the phonon one. In unordered solid solutions this component is, as a rule, lower than in pure metals. This indicates that scattering of phonons on impurities in such alloys is significantly more intense than phonon—phonon scattering (for the temperatures considered λ_p depends in practice on only these two forms of scattering).

In unordered solid solutions the atoms occupy fully defined positions in the crystalline lattice, but translational symmetry in the position of atoms of various types is disrupted. The atomic masses and lattice constants vary from lattice point to lattice point, which causes additional phonon scattering. At low impurity concentrations the increase in phonon thermal resistance $\Delta W_p \sim \Delta r$, where Δr is the difference in atomic dimensions of the impurity and basic metal atoms. At large impurity concentrations the distorted spheres of adjacent impurity ions overlap, which causes a retardation in the decrease in thermal conductivity and attainment of a practically constant value.

Thus, to decrease λ_p metals must be used which have force constants differing greatly from the force constants of the matrix. The magnitude of the forces holding atoms together in pure metals can be estimated by comparing such properties as fusion temperature, strength, compressibility, thermal expansion coefficient, and lattice period.

With consideration of the above factors, those elements which would have the greatest effect on nickel thermal conductivity were determined. These proved to be chromium, tungsten, molybdenum, rhenium, gallium, and germanium. The first five of these are transition metals, which have a high scattering section; the mean energy of their d shells is close to the Fermi level of nickel E_{FNi} = 9.207 eV; E_{dV} = 8.130 eV; E_{dCr} = 8.010 eV; E_{dW} = 9.450 eV [15, 16]; moreover, they have a high Fermi energy (higher than nickel) E_{FCr} = 11.682 eV; E_{FMo} = 10.948 eV; E_{FV} = 10.363 eV [16]. The force constants of tungsten, molybdenum, and rhenium, as well as gallium and germanium differ most greatly from those of nickel.

A number of industrial alloys of nickel with the doping elements mentioned were studied. The thermal conductivity wasmeasured with an ITEM-1M instrument, which uses the quasisteady-state monotonic heating method [2].

The studies performed established the degree of influence of nickel alloy components on thermal conductivity as follows (in order of decreasing effect): vanadium, chromium, tungsten, gallium, rhenium, molybdenum, and germanium. It was also found that the lowest thermal conductivity of the alloys tested occurred in chrovangal [17]. At standard composition of this alloy it was possible to produce a thermal conductivity of 7.5 W/(m·K). A similar analysis performed for titanium found a number of industrial alloys with thermal conductivities in the interval 6.5-7.0 W/(m·K).

NOTATION

λ, thermal conductivity, W/(m·K); λ_e, electron component of thermal conductivity, W/(m·K); λ_p, phonon component of thermal conductivity, W/(m·K); W_e, electron thermal resistance; W_o, electron thermal resistance produced by scattering on impurities and defects; W_i, electron thermal resistance produced by electron—phonon scattering; ΔW, deviation from additiveness; n, number of impurity atoms per unit volume; E_F, Fermi energy, eV; $Q_i(E)$, section for scattering on impurity atom; E_d, mean energy of d shell, eV; Δr, difference in atomic dimensions of impurity and basic metal atoms.

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