Baikov Institute of Metallurgy and Materials Science RAS

Physicochemical principles of the development of rhenium-based and rhenium-containing alloys

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Introduction

This report is devoted mainly to the problems of the development of rhenium-based structural materials and rhenium-containing high-strength alloys, including the alloys for high-temperature service.

This report does not concern the characteristics of rhenium materials such as chemical and physical properties, which allow one to design unique catalysts, emitters, thermocouples, and other materials with special properties.

Rhenium (Re) - hcp transition metal Group VII of the third long period of the periodic table (A 75).

Rare element: weight clarke is ~10^{-7}- 10^{-6} %

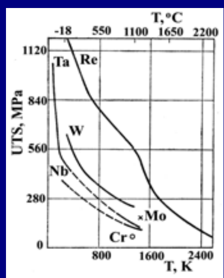
Physical properties

- T_{melt} = 3453 K (> T_{melt} refractory metals, < T_{melt} W)
- T_{vap} = 6173 K (> T_{vap} refractory metals, < T_{vap} W)
- Vaporization rate 8.41·10^{-6} g/m² at 3000 K in vacuum).
- $T_{operating}$ (weight loss < 1% after 10 h) ≤ 1910°C for Mo,
  ≤ 2380°C for Re,
  ≤ 2560°C for W
- λ = 71,2 W/m·K (>λ refract. metals, in 2, 3, 5,5 times < λ Mo, W, Cu)
- Self-diffusion coefficient ~ 10^{-11} – 10^{-16} at 2700-2100 K, close to D of W and Ta, < D of other metals
- Density ρ = 21,04 g/cm³ (< ρ Os, Ir, Pt)
- Young modulus E= 460-510.3 GPa (>E refract. metals, < Ru, Os, Ir)
- Low thermal expansion coefficient α_t= 6,2·10^{-6}, K^{-1} at 293 K^{-1}
- High specific electrical resistance ρ=17,2-22,8 mk Ω·cm at 273K
  (in dependence of the purity, alloying and degree of deformation)

Mechanical properties of Re

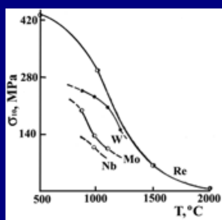
Short-term strength

- Wire Ø 1.27-1.6 mm:
  at RT UTS= 1200 MPa, El = 25% (as recrysallyzed)
  UTS= 2300 MPa, El = 2.5% (as deform. ε = 15%)
- At elevated temperatures (at least, up to 3000 K)
  Re surpasses both refractory V- and VI-group *Me* and noble refractory *Me* VIII-group (Ir, Rh, Os, and Ru):
  At 1600 and 2000 K, Re has UTS of 360 and 200 MPa.
  At 1600°C W, Mo, Ta, Nb have UTS 200, 180, 100, 90 MPa.
  At T≤2000-2400 K
  UTS Re ≤ UTS modern bcc W and Mo alloys with Re, *Me*C.
  At 2400 K ≤ T ≤ 2950 K UTS >50 MPa (Re),
  10-15 MPa (W),
  50-100 MPa (W-Re-*Me*C)



Long-term strength

The long-term (10 h) strength of Re is higher than those of unalloyed W, Mo, Nb, and Ta at least up to 3000 K
Re: σ_{10} = 19 MPa at 2500°C



Ductility

- At RT and up to cryogenic temperatures Re has high ductility and surpasses bcc cold-brittle refractory VI-group *Me*
  Re insensitive to thermal shock and to thermal cycling (100 000 thermal fatigue cycles 290-2500 K)

(E.K.Ohriner, B.Reed, J.Biaglow, R,H,Tuffias S.Schneider, M.A.Appel, J.C.Carlen, J.W.Pugh)

Applications for rhenium products

Applications for products of rare metal Re (PM/CVD) under extreme thermal and mechanical stresses are determined by very high melting point, good high temperature strength and low temperature ductility.

450 N chamber. Starting material Re rod Ø 110 mm

(J.C.Carlen,, M.A.Appel)

Real and perspective applications

In space probes

- Reusable rocket thrusters, liquid rocket combustion chambers
- Radiation-cooled rockets
- Energy generation using thermionic techniques.
- Re surfaces are coated by oxidation resistant Ir (CVD / ED) to resist the O_2 - containing combustion gases.
- Fuel cladding in SP 100 Space Power System Re/Ir increases $t_{operat.}$ up to 2200°C instead of 1370°C for Nb-1%Zr alloy.
- Missiles and other military equipment.

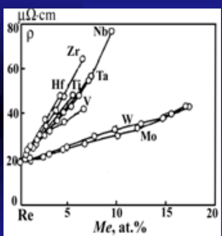
Industry, scientific instruments

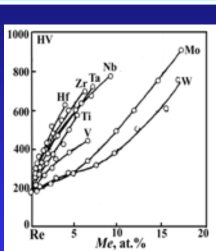
e.g. high-temperature thermocouples, electrical contacts with a low contact resistance, electrodes in X-ray tubes, high energy electronic devices, filaments in mass spectrometers, etc.

Alloying of rhenium

Re is characterized by high work hardening and poor workability.

Re (PM / ZEBM) may be deformed to ε = 25 / 45% (respectively) without failure. Under industrial conditions, Re may be subjected to cold rolling or drawing to ε=10-15% between intermediate annealings without cracking.





The long and tedious production route of Re make Re a very expensive material.

Solid-solution alloying of Re increases its low- and medium- temperature hardness and strength, decreases ductility the higher, the larger is ΔR (atomic radii of Re and AE) and the higher are the distortions of rhenium crystal lattice due to the alloying (IV and V group *Me)*. All AE decrease T_{melt} Re

There are no AE for Re to eliminate its workability and mechanical properties

At RT:	Re (VAM)	Re-5Mo	Re-5W	Re-10W
UTS, MPa	700	850	1020	1020
El, %	25	12	20	8.5

Alternative materials have been sought and developed.

In these materials Re is used as alloying element (AE)

The physicochemical approaches to the design of structural alloys with Re

Use of Re as AE or as alloy base is determined by 2 main factors:
- the mutual solubility of Re and AE and
- four "rhenium effects", which have no analogs

«Re effect-1»: High solubility of Re in bcc VI-Group bcc *Me* (W, Mo and Cr), addition of 25-35 at.% Re simultaneously increases low-temperature ductility and strength of cold-brittle VI Group metals (J.Hughes and G.Geach)

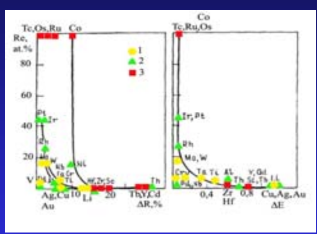
«Re effect-2»: the unique ability of 25-35 at.% Re to increase strain-hardening rate of the VIA-Group bcc *Me* (E.Savitskii, M.Tylkina, Z.Petrova, K.Povarova)

«Re effect-3»: ability of 2-8 at.% Re to increase low-temperature ductility of W and Mo alloys (K.Povarova, V. Trefilov, EU. Milman)

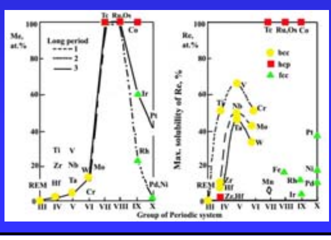
«Re effect-4»: ability to increase the high-temperature strength and service life of modern nickel-base superalloys

Specific Features of Interaction of Re with Transition Metals (1)

Solubility of Re in *Me* in dependence of ΔR and ΔE



Solubility of *Me* in Re and Re in *Me* in dependence of position of *Me* in Periodic system



Maximum solubility of *Me* in Re and Re in *Me* is determined by:
- *Me* crystal lattice,
- difference in atomic radii, ΔR
- difference in electronegativities, ΔE
- position of *Me* in Periodic system.

Solubility of *Me* in hcp Re is generally lower, then higher are the ΔR and ΔE values.

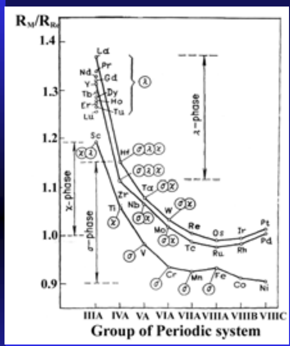
For the same ΔR and ΔE values, solubility in hcp Re of fcc metals is up to 43% higher than that of bcc metals (below 16%).

Solubility of fcc and bcc *Me* in hcp Re abruptly decrease as ΔR ≥ 5% and ΔE ≥ 0.1

Solubility of Re in bcc *Me* is high: 37-65 %. It surpasses the Re solubilities in fcc *Me* and hcp modifications of Ti, Zr, and Hf.

These data are the base to choose limited concentrations of Re as AE in *Me*-based solid solutions

The Specific Features of the Interaction of Rhenium with Transition Metals (2)



The type of the IC depends on dimensional (R_{Me}/R_{Re}) and electrochemical (ΔE) factors determined by the position in Periodic system and by the electronic structure of the *Me*.

Intermetallic compounds (IC) in the systems of Re with transition *Me* predominantly belong to three types: λ, σ, and χ phases.

In the systems with *Me* of long period	1	2	3
III group	λ, χ		
IV group	χ	λ, σ, χ	
V-VI group	σ	σ, χ	
VIII group	σ / no IC	no IC	

These phases may be formed in alloys with Re content higher limit solubility of Re in *Me*

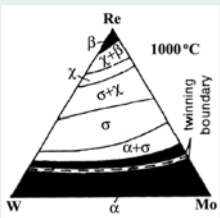
Re does not form intermetallic comounds with *Me* of VII group (e.g. Os, Ir, or Ni)

Re does not form stable interstitial phases

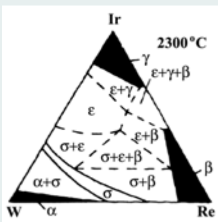
Phase diagrams as a base for Re-alloys development

Interaction of Re with 64 elements is known, 100 complete or partial binary and ternary phase diagrams are constructed

W-Mo-Re



Re-Ir-W



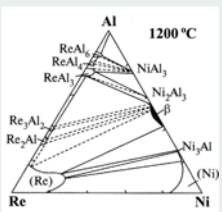
Re-containing W, Mo, W-Mo alloys

W and Mo are bcc cold-brittle refractory *Me*
Characterized by low solubility Of interstitial elements

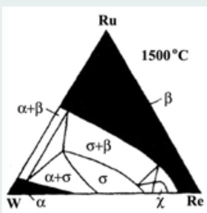
Ir-covered Re devices

No brittle IC on Ir/Re boundary

Re-Ni-Al



W-Ru-Re



Ni-based superalloys,

- High solubility of refractory Re in Ni-based s.s.
- Possibility to substitute part of Re by Ru in Ni superalloys (density and T_{melt} Ru is lower those of Re)

The physicochemical approaches to the design of structural alloys with Re

Use of Re as AE or as alloy base is determined by 2 main factors:
- the mutual solubility of Re and AE and
- four "rhenium effects", which have no analogs

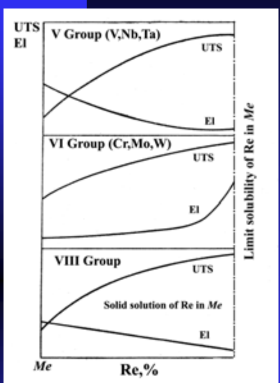
«Re effect-1» - high solubility of Re in bcc VI-Group bcc *Me* (W, Mo and Cr): addition of 25-35 at.% Re (near solubility limit of Re in *Me*) simultaneously increases low-temperature ductility and strength of cold-brittle VI Group metals (J.Hughes and G.Geach)

«Re effect-2»: the unique ability of 25-35 at.% Re to increase strain-hardening rate of the VIA-Group bcc *Me*
(E.Savitskii, M.Tylkina, Z.Petrova, K.Povarova)

«Re effect-3»: ability of 2-8 at.% Re to increase low-temperature ductility of W and Mo alloys (K.Povarova, V. Trefilov, EU. Milman)

«Re effect-4»: ability to increase the high-temperature strength and service life of modern nickel-base superalloys

«Re effect - 1»



W-27%Re

Mo-47%Re

Deformation twins

High solubility of Re in cold-brittle bcc VI-group *Me* (W, Mo and Cr).
Addition of 25-35 at.% Re simultaneously increases strength and low-temperature ductility of cold-brittle VI Group bcc *Me* Addition of 25-35 at.% Re decrease T_{melt} W, Mo, Cr

New class of high-temperature alloys and alloys with special physical and chemical properties: VM and PM alloys (wt.%): W - (25-30)Re, Mo - (45-50)Re, and W – 18Mo - 25Re

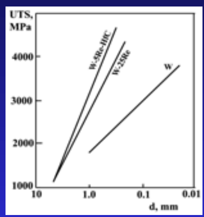
<u>Different versions of the explanation «Re effect-1»</u>

1. Alloying with Re changes electronic structure of bcc VI-group *Me*, increase the state density near Fermi surface.
2. Decrease in the Peierls-Nabarro stress level.
3. Addittional mechanism of deformation. The deformation twins indicating the appearance of the «Re effect-1» in the alloys containing >23 at. % Re.
4. Re increases the solubility of interstitial impurities in *Me* s.s., and decreases their tendency to segregate at grain and subgrain boundaries, lattice defects.
Re segregates at grain and subgrain boundaries, ousting interstitial elements, e.g., carbon.
5. Change in composition and improvement in the morphology of oxide and carbide precipitates.

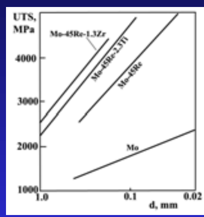
«Re effect - 2»

The unique ability of Re
to increase strain-hardening rate
of the VIA-group *Me*

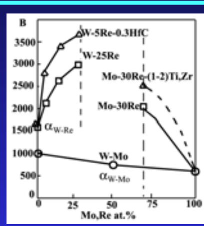
High-strength alloys:
high-Re solid solutions W-Re,
Mo-Re, and W-Mo-Re



σ_u
MPa



B



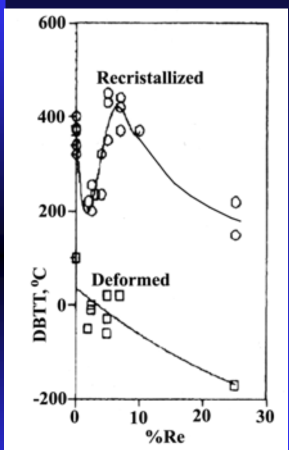
<u>The strain hardening</u> is realized in the W(Mo)-Re solid solutions due to their deformation at $T_{d/b}$ >T < $T_{recryst}$. This causes the formation of fine structure with elongated grains ("fibers"), cells of below Ø ~0.1 µm, and high dislocation density (up to 10^{12}-10^{14} cm^{-2}).

Increase in strength upon deformation may be expressed by the equation

$$\sigma_u = A - B \cdot \lg d,$$

d is Ø of rod (wire) in mm and A is the UTS (σ_0) of the wire Ø 1 mm.
The coefficient B reflects an intesity of increase in strength upon deformation.
B increases with increasing Re content in W (Mo) alloys.
Fine particles (<100nm) of the strengthening phases (ZrC, HfC) increases the ability of W(Mo) to strain hardening.

«Re effect - 3»



The unique ability of low Re content to increase low-temperature ductility and decrease $T_{d/b}$ of recrystallized W and Mo alloys

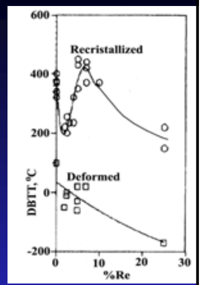
New class of high-temperature
low Re structural alloys :
VM and PM
W-(2-4) wt. % Re, Mo - (6-8) wt. % Re

Re content < 5% and > 10% differently affects the electronic structure of the W-Re solid solutions: distributions of W and Re electrons near the lattice points are different. This affects the values of the binding energy of impurity atoms with dislocations and other lattice defects, stacking-fault energy, etc.

Nature of Re effect-1, 3

Unique ability of 2-4 and 25-30 at.% Re to increase low-temperature ductility and decrease $T_{d/b}$ of cast and recrystallized W and Mo alloys («Re effect-1» and «Re effect-3»)

The constitution of the valence zone of W-Re s.s. with bcc unordered crystal lattice is complicate. Re content < 5% and > 10% differently affects the electronic structure of W-Re s.s.: distributions of W and Re electrons near the lattice points are different. This affects the values of the binding energy of impurity atoms with dislocations and other lattice defects, stacking-fault energy, etc.

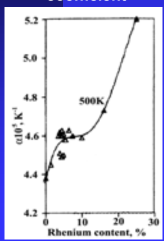


Comparison of ESCA spectra and anomalous concentration dependences of some properties of the W-Re solid solutions show: the alloying with rhenium in these range of contents (5-8%) should be avoided in alloy design because of the instability of many of properties.

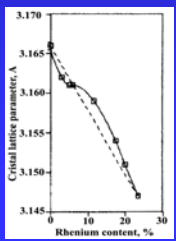
We develop 2 group of alloys on the base W-4Re and W-(25-27)Re

Anomalous concentration dependences of properties of W-Re s.s.

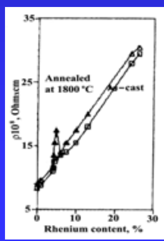
Thermal expansion coefficient



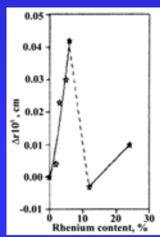
Cristal lattece parameter



Electrical resistance

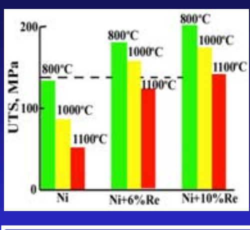


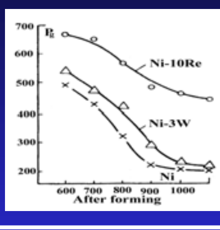
Electron/positron annihilation



«Re effect - 4»

The ability to increase the high-temperature strength and service life of modern nickel-based superalloys





Effect of Re (wt.%) on the high-temperature properties of Ni was investigated in1970-th:
- UTS at 800, 1000, and 1100ºC
- Stiffness of the cathode bases Ni-Re alloys

(M.A.Tylkina, E.P.Arskaya, IMET RASc.)

E.N.Kablov,R.W.Brumfeld, D.A.Ford, M.C.Tomas, D.J.Friser

Re containing high γ´ nickel-base superalloys.

Family of nickel-base single crystal alloys type of ZchC-32, CMSX-10 with 3.6-10 wt % Re have higher mechanical properties (strength, stiffness, time to failure) as compared to the rheniumless Ni alloys (with tungsten and other AE – REM, Zr, Hf, Ta).

Modern high-temperature structural superalloys of complex compositions (γ + γ′) with 2-9 wt. % Re

Re strengthens the nickel-based γ solid solution, increases the time to failure in tens times, and allows one to elevate the operating temperatures of the alloys for blades (including those produced by directional solidification) for advanced gas-turbine engines up to 1100°C (turbine inlet temperatures will approach 1650°C)

Refractory Re strengthens γ phase and decreases the diffusion rates in volume and at grain boundaries and γ′ / γ interphase interphases.

Conclusion

This report is devoted mainly to the problems of the development of rhenium-based structural materials and rhenium-containing high-strength alloys, including the alloys for high-temperature service.

This report does not concern the characteristics of rhenium materials such as chemical and physical properties, which allow one to design unique catalysts, emitters, thermocouples, and other materials with special properties.

In many aspects, the use of rhenium structural alloys depends on the improvement of technological processes for their preparation and processing. Sometimes it is difficult to effectively select the production process for rhenium-containing material because the allowances should be made for the required combination of properties, destination, shape and dimensions of the product, stabilities of composition, structure, and properties upon variations of the processing parameters, and the economic feasibility and accessibility of one or another production method.

It should be also taken into account that the unique potentialities of rhenium and rhenium alloys may be most completely realized on the condition of an optimal structural state formed in the material by deformation and / or heat treatment. This is of special importance for Mo-Re and W-Re alloys.