Contact materials used for electrical breakers are often made with silver alloys. Mechanical and thermodynamical properties as well as electron emission of such complicated alloys present a lack of reliable and accurate experimental data. This paper deals mainly with electron work function (EWF) measurements about silver–metal (Ag–Me) electrical contacts (Ag–Ni (60/40) and Ag–W (50/50)), before and after surface heat treatments at 513 K–873 K, under UHV conditions (residual gas pressure of $1.4\times 10{-}7$ mbar). The electron work function (EWF) of silver alloyed contacts was measured photoelectrically, using both Fowler's method of isothermal curves and linearized Fowler plots. An interesting fact brought to light by this investigation is that after vacuum heat treatments, the diffusion and/or evaporation phenomena, affecting the atomic composition of the alloy surface, somehow confine the EWF of the silver–nickel alloy, Φ(Ag–Ni), determined at room temperature in interval]Φ(Ag), Φ(Ni) [=] 4.26 eV, 4.51 eV[. Surface analysis of two specimens before and after heating showed a significant increase of tungsten atomic proportion on the contact surface for Ag–W contacts after VH treatments. A multilayer model, taking into account the strong intergranular and volume segregation gives a good interpretation of the obtained results