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ABSTRACT

Long-term high-temperature measurements in nuclear environments have long posed difficult problems. The tungsten-rhenium alloy thermocouples typically used in such applications undergo large decalibrations resulting from nuclear transmutation of the component materials. An alternative thermocouple, comprising pure molybdenum and niobium thermoelements, is virtually immune to transmutation effects, but is limited in utility by other properties. Thermocouples composed of molybdenum-niobium alloys show promise of significant improvement over the pure-metal combination. The W-Re decalibration problem is detailed, and the status of Mo-Nb thermocouple development reviewed, including recent efforts at the Idaho National Engineering Laboratory.

INTRODUCTION

Stable, reliable high-temperature measurements are a high priority for space based nuclear power systems. Although a variety of high-temperature instruments exist, thermocouples offer some distinct advantages for such measurements by virtue of their passive nature and simplicity of operation. Thermocouples, in contrast to other instruments, require no external excitation source and produce an output voltage that is converted directly to temperature without the use of algorithms or other computation. Thermocouple measurements are intrinsically differential, and this property can be used to advantage for differential measurements.

The key temperatures in space nuclear power systems are above 1300 K, a region where standard thermocouple types fall short of meeting the necessary criteria. The tungsten-rhenium alloys provide ample temperature range, but are subject to severe decalibration due to nuclear transmutation of the component materials. Nickel-based alloys, such as Chromel and Alumel or Nicrosil and Nisil, are generally regarded as sufficiently insensitive to nuclear effects (see Kelly et al. 1962, for example), but lack the required temperature range. Intermediate types, such as platinum-rhodium or platinum-molybdenum alloys, combine marginal temperature range with moderate transmutation effects (Ehringer et al. 1966).

Much effort has been expended in attempts to correct temperature data from W-Re thermocouples that have decalibrated as a result of nuclear transmutation. In general, these efforts have met with limited success at best, but, lacking a suitable alternative, such attempts have continued. A molybdenum-niobium thermocouple, however, which combines high-temperature capability with low neutron capture cross sections, and hence negligible transmutation, has attracted attention for over two decades as a candidate for nuclear applications. In the following pages, the problems arising from transmutation of W-Re thermocouples are considered and the status of Mo-Nb thermocouple development is reviewed.

TUNGSTEN-RHENIUM THERMOCOUPLE DECALIBRATION

Tungsten-rhenium alloy thermocouples have been widely available since the mid-1960s, and have been used successfully for temperature measurement to at least 2500 K in inert atmospheres. Long-term use in nuclear environments presents special decalibration problems, however. Tungsten, with an average thermal neutron cross section of 18 barns, transmutes under nuclear irradiation to rhenium (σ= 86 barns), which itself transmutes to osmium. For example, Browning and Miller (1962) calculated that 19% of a tungsten sample and 91% of a rhenium sample would be transmuted by a thermal neutron exposure of 3 x 10^{22} neutrons/cm^2 (nvt). W-Re alloys thus become W-Re-Os alloys whose composition changes with irradiation exposure, that is, as a function of time. Accompanying this compositional change is a calibration change, or decalibration.

To the time-varying thermocouple composition must be added the effect of the spatially-varying composition in the region of the neutron flux gradient. The extent of thermocouple decalibration depends not only on the degree of radiation-induced composition change, but also on the relative position of the temperature and neutron flux gradients. Three such relative positions are illustrated in Figure 1. If there is no neutron flux within the region of temperature gradient, where the thermocouple's electromotive force (emf) is generated (Fenton 1980), there is no compositional change in that part of the thermocouple, and no thermoelectric decalibration occurs (Figure 1a). If the two gradients partially or completely overlap (which is the case in most real situations), then a section of transmuted thermocouple lies within the temperature gradient and the calibration changes in proportion to the extent of gradient overlap (Figure 1b). If the temperature gradient lies entirely within a region of high constant neutron flux, then all of the signal-generating portion is uniformly transmuted and the thermocouple decalibration is the greatest of any relative position (Figure 1c).

In general, each irradiation experiment has a unique combination of temperature and neutron flux profiles and their relative positioning. In addition, neutron flux spectra vary from one test facility and experiment to another. These parameters are often known inexactly, if at all. Thus, it is not surprising that only approximate temperature corrections have resulted from test data correlations.

Irradiation test results compiled by Walter (1974) revealed typical W-Re thermocouple decalibrations within the range of -10% to -25% for thermal neutron fluences of 2 x 10^{21} nvt and fast fluences of the same order. Interpretation is complicated by the fact that thermal, epithermal, and fast neutron fluences vary from test to test, and the contributions of each are not easily separated. It seems safe to conclude, however, that the largest contribution is that from thermal neutron irradiation, in view of the low capture cross sections for fast neutrons. Vitanza and Stien (1986), reviewing many of the same experiments, noted that the data fell into two groups: one with an average decalibration of $-11.0\%/10^{21}$ nvt, the other averaging $-5.0\%/10^{21}$ nvt, a difference that may be due to the types of reference measurement employed. Their entire data base was covered by a decalibration band of -3% to $-15\%/10^{21}$ nvt, compared with a decalibration band of -6.7% to $-10.4\%/10^{21}$ nvt for separate data obtained in their own tests at Halden, Norway.

Johnson and co-workers (1974) compared their irradiation results with the calibration data for a series of fabricated alloys simulating various stages in the transmutation process of W-Re thermocouple alloys (Pratt 1968). They found only qualitative agreement between the two data sets, although extrapolation appears to predict better quantitative agreement at fluences greater than 3 to 5 x 10^{21} nvt (Ara et al. 1986).

Other factors besides differences in temperature gradients and neutron flux profiles and spectra can affect the degree of decalibration. Thermocouples sheathed in rhenium tubes, or insulated with hafnium oxide, for instance, will be shielded somewhat by these high-cross section materials, as opposed to instruments having, for example, molybdenum sheaths and aluminum oxide insulation. The thermocouple size and, consequently, the volume of sheath and insulation materials surrounding the thermoelements can also be a factor in the case of high cross section materials. The effects of phase separation of osmium in transmuted W-Re alloy wires (Skaggs et al. 1967), and of transmuted impurities in the insulating material have not been studied. They may produce minor, but variable and undetermined, contributions to decalibration.

There is no consensus among investigators on a number of other key points such as the relationship between operating temperature and decalibration, the existence of a threshold neutron fluence below which decalibration is not evident, and the contribution of epithermal and fast neutrons to transmutation. Little is known about the quantitative thermoelectric effects of vacancies and dislocations produced by fast neutron irradiation.

In short, twenty years of using W-Re thermocouples in nuclear environments have failed to produce a method of applying anything more than a first-order correction factor to radiation-induced decalibration data. That is a small wonder in view of the myriad factors involved and the staggering complexity that follows.

PURE Mo VERSUS PURE Nb THERMOCOUPLES

Molybdenum and niobium, with melting points of 2873 K and 2741 K and thermal neutron capture cross sections of 2.5 and 1.1 barns, respectively, have been studied by Fanciullo (1964), Pletenetskii (1967), Zysk and Robertson (1971), and Schley and Metauer (1982), among others. Figure 2 shows the temperature-emf findings of various studies, including one at the Idaho National Engineering Laboratory (INEL).

The magnitude of the Mo-Nb thermocouple signal is sufficiently large to be viable as a high-temperature thermocouple. However, the low sensitivity above about 1800 K causes concern about the thermocouple's utility in that temperature range. In the INEL study, for example, the average sensitivity between room temperature and 1800 K was 12.23 μV/k, but from 1800 K to 2300 K it was 2.14 μV/K and from 2100 K to 2300 K only 0.39 μV/K. These values vary from those of other studies and may be lower in part because the tests were conducted on small-diameter (less than 0.25 mm) wires. An important feature of Figure 2 is the discrepancy among the curves. This may be simply a manifestation of the lot-to-lot variation in thermoelectric characteristics noted by nearly all investigators.

Other properties of pure-metal Mo-Nb thermocouples that have tempered enthusiasm for their use in nuclear applications include the effect of wire size on calibration and drift, sensitivity to contamination (which also produces drift), and high-temperature embrittlement. For example, we noted a change of -9.6% in the thermoelectric output of a Mo-Nb thermocouple after two hours, and of -12.7% after four hours, at 2200 K. When held at 2000 K, the corresponding changes for an identical thermocouple were -7.5% and -10.1%, respectively. In the latter instance, the drift noted after a preconditioning period at 2200 K did not exceed -0.3% during four hours. These figures are somewhat greater than those reported by Schley and Metauer (1982), in all probability again reflecting lot-to-lot materials variations. There is evidence indicating that the majority of this drift is due to crystalline changes in the molybdenum thermoelement (Schley et al. 1980).

Nevertheless, during an in-pile test at Grenoble, France, comparing the performance of W-Re alloy, Pt-Rh alloy, Pt-Mo alloy, and Mo-Nb thermocouples (Schley and Metauer 1982), the Mo-Nb instruments showed the smallest decalibration (and that was perhaps attributable to effects independent of irradiation), and operated the longest before failing. Encouraged by these results, the French group undertook a systematic study of Mo-Nb alloys as thermocouple materials. Above all, they looked for alloys with greater thermoelectric output and temperature sensitivity. The attenuating effect of alloying upon grain growth in pure metals is well known, and reduced brittleness and sensitivity to contamination might also be anticipated as a result.

MOLYBDENUM-NIOBIUM ALLOY THERMOCOUPLES

Based on the empirical observations of Crussard (1948), Schley et al. (1981) fabricated bulk samples (6 x 6 x 8 mm) of a series of Mo-Nb alloys and determined the absolute thermoelectric power of each as a function of temperature (Figure 3). From this information, they constructed the temperature-emf curves of the best combinations of these alloys. Two such combinations, Mo-5%Nb versus Nb-10%Mo and Mo-5%Nb versus Nb-40%Mo, had significantly higher thermoelectric outputs than the others. These are shown in Figure 4, along with pure Mo versus pure Nb and W-5%Re versus W-26%Re for comparison. Of the two, Mo-5%Nb/Nb-10%Mo was deemed to be better, despite its lower emf at high temperatures, because of its greater temperature sensitivity between 1800 K and 2300 K and because it was believed to be a more easily fabricated alloy.

Fabrication of small-diameter wires of these promising alloys proved to be difficult. Hot-working of arc- and electron beam-melted billets was only partially successful (Glock et al. 1978). Unfortunately, lagging interest in this thermocouple in France resulted in discontinuance of work on its development, and plans to use alternate wire fabrication techniques were thus not carried out.

We have attempted to take up development of these alloys at the INEL, for potential application to space reactor temperature measurement. Powder metallurgy methods have met with only limited success to date, attaining wire diameters of about 2 mm in the initial attempts. Direct application of molybdenum manufacturing methods has not proved to be adequate, and elimination of oxidation during all stages of fabrication appears to be a key factor in successful billet reduction. Significant progress has been noted with successive iterations, however, and continued progress is anticipated. The immediate goal of this work is to produce wires small enough (0.1 to 0.5 mm in diameter) to be of use in standard-sized sheathed thermocouples.

CONCLUSIONS

Present thermocouple technology is inadequate to provide instruments that are capable of making accurate, reliable, long-term temperature measurements in applications that include space nuclear power systems. Standard high-temperature W-Re alloys suffer significant transmutation and thermoelectric decalibration, and other standard thermocouples lack the necessary temperature range and radiation immunity for such applications. Thermocouples composed of pure Mo and Nb are virtually insensitive to transmutation effects, but are limited by contamination and drift and lack the desired temperature sensitivity above 1800 K.

Highly promising alloys of Mo and Nb, originally developed in France, offer significant improvements over the pure-metal combination, but did not reach the application stage before development was discontinued. Work at the INEL has been directed toward producing small-diameter wires of these alloys for use in standard thermocouple configurations. Although that goal has not yet been attained, there has been progress toward it; once achieved, full metrological characterization of the Mo-5%Nb/Nb-10%Mo thermocouple will be undertaken and its application in nuclear systems explored.

The present lack of radiation-resistant thermocouples for high-temperature nuclear applications may turn attention to other measuring devices. However, ultrasonic thermometers, except those having molybdenum or niobium sensing elements, suffer radiation-induced decalibration from transmutation, much as W-Re thermocouples do. The same is true of resistance thermometers with non-standard materials intended to extend their measurement range beyond the 900 K conventional RTDs. Only the inherently complex technique of Johnson noise power thermometry, by virtue of being independent of the sensor's composition and resistance, presently appears capable of accurate long-term operation in nuclear environments.

A new fiber optic thermometer is available with an upper temperature limit of about 2200 K, but the user must deal with radiation-darkening of the optical fibers and the resultant signal loss.

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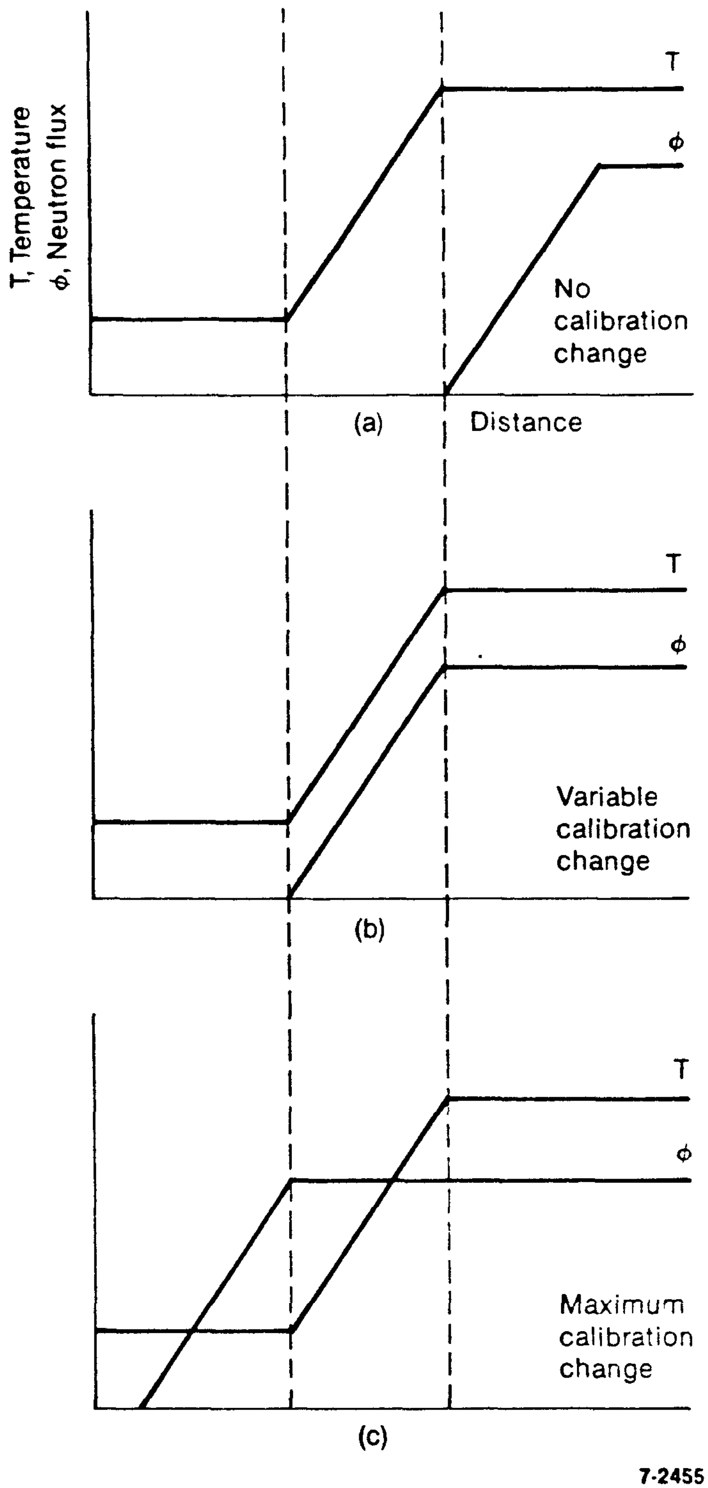

FIGURE 1. Relative Position of Temperature and Neutron Flux Gradients (adapted from Browning and Miller 1962.)

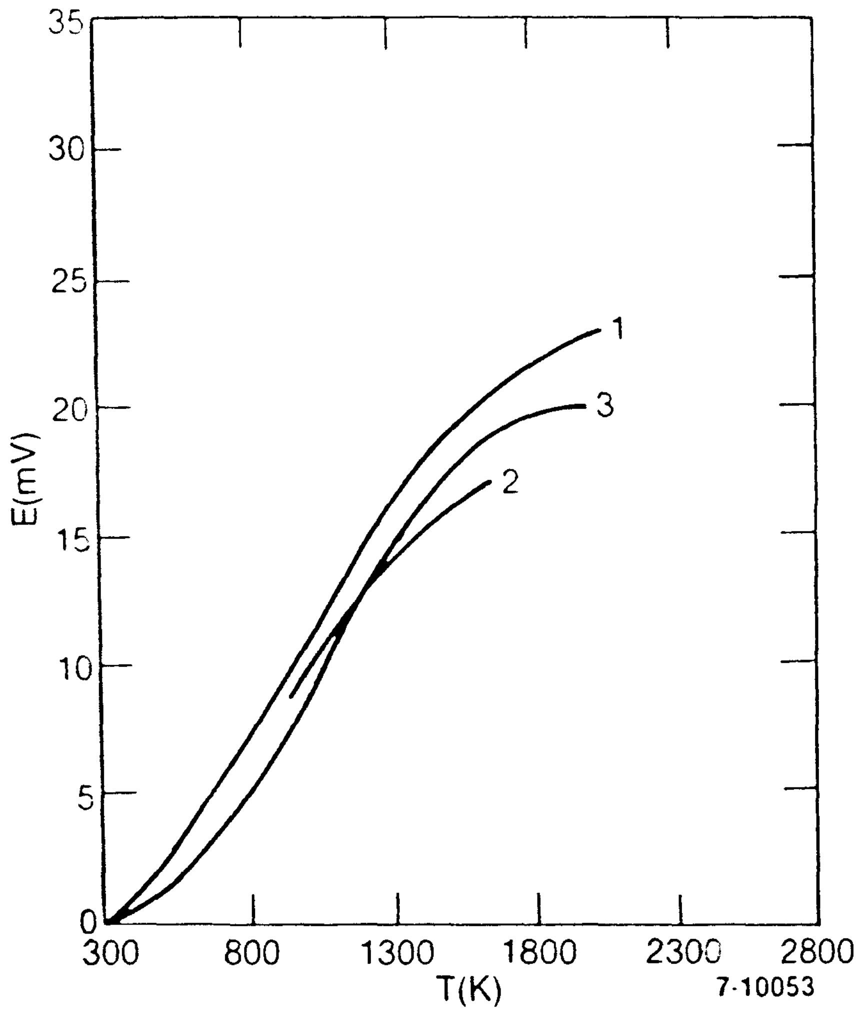

FIGURE 2. Temperature-Emf Curves for Mo-Nb Thermocouples in Various Investigations: (1) Pletenetskii (1967), (2) Fanciullo (1964), and (3) INEL.

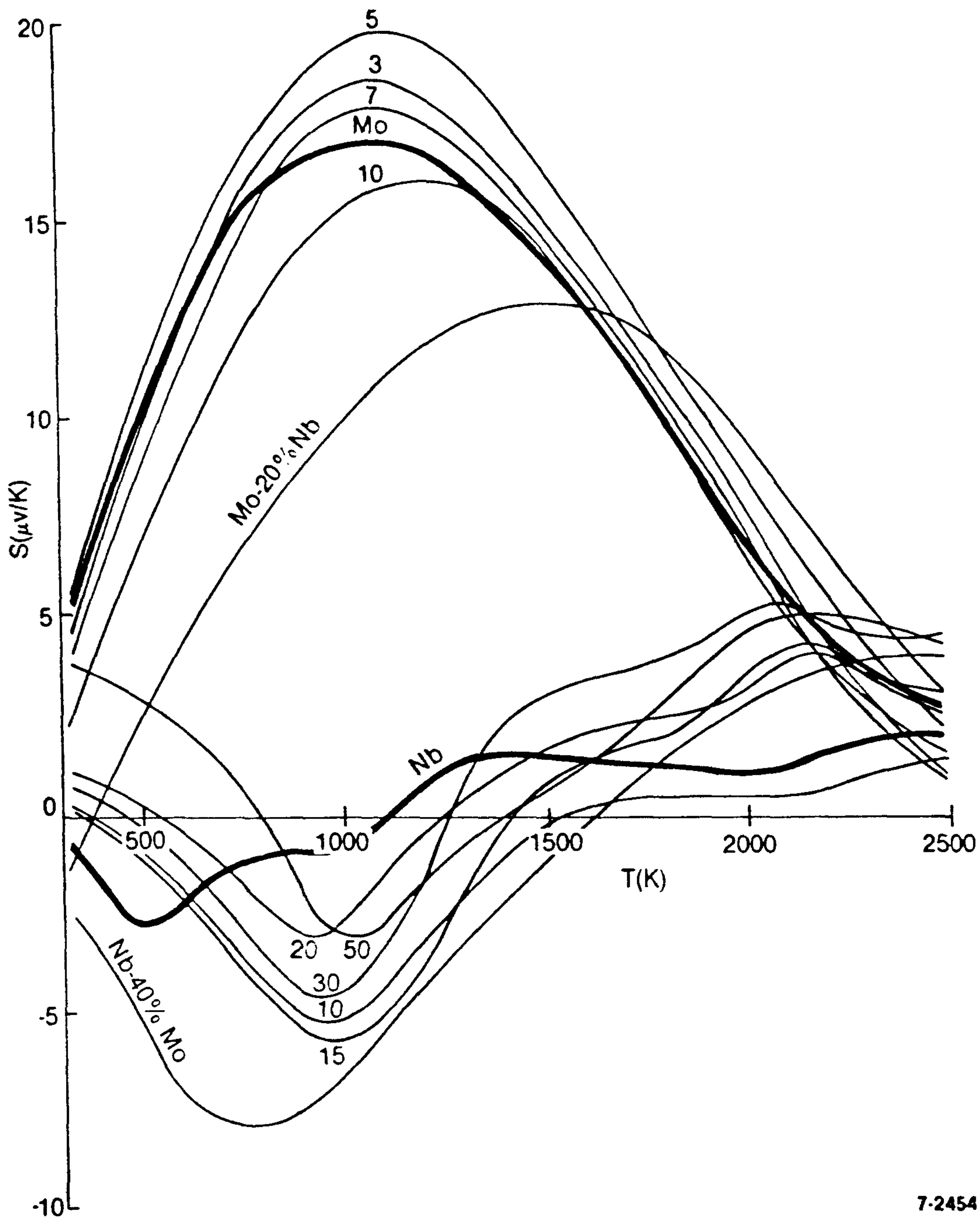

FIGURE 3. Absolute Thermoelectric Powers of Mo, Nb, and Mo-Nb alloys(from Schley and Metauer 1982).

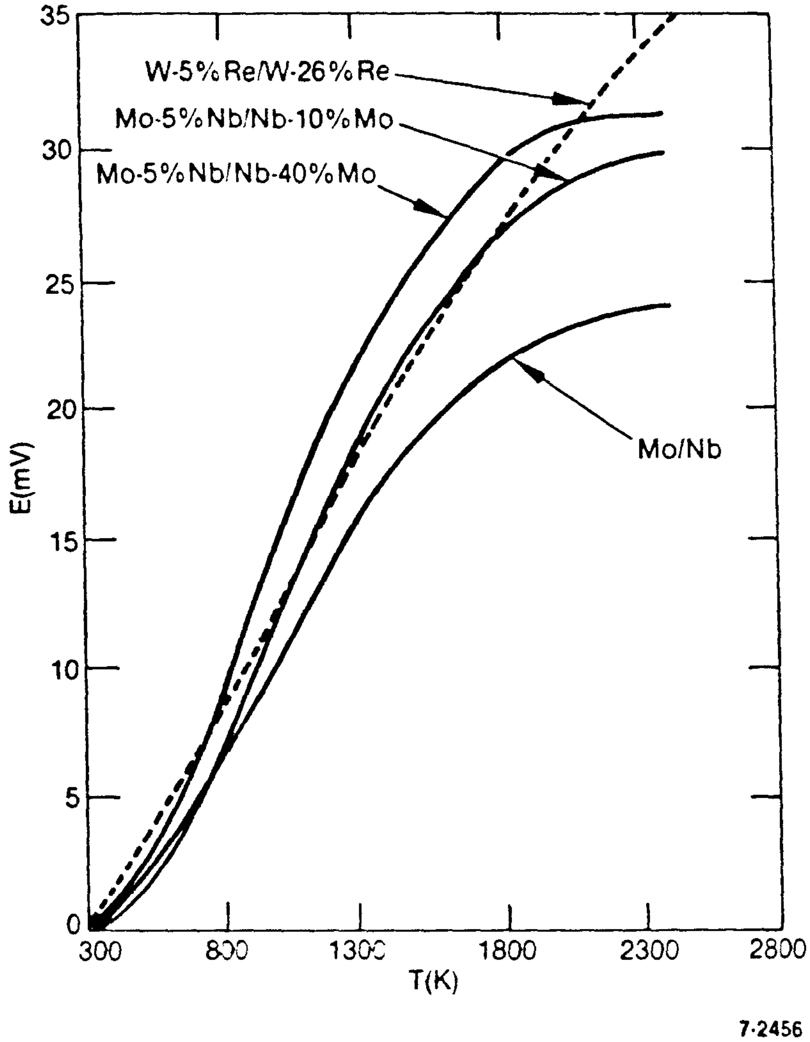

FIGURE 4. Comparison of Temperature-Emf Curves for Pure Mo versus Pure Nb, Mo-Nb Alloy, and W-Re Alloy Thermocouples.