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Thermal Expansions Of Kovar And Ceramvar And Seals Of These Materials To Alumina

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THERMAL EXPANSIONS OF KOVAR AND CERAMVAR AND SEALS OF THESE MATERIALS TO ALUMINA

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ABSTRACT

Thermal expansions of Ceramvar and Kovar were measured over the range of -180 to + 1000°C. These measurements aid in predicting thermal contraction mismatch stresses of Ceramvar- or Kovar-to-alumina seals. These stresses reach a maximum during cool-down from the braze temperature: and it is they, rather than room-temperature residual stresses, which are the limiting factor in sealing. The technique of making "moly-manganese" seals is reviewed briefly.

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THERMAL EXPANSIONS OF KOVAR AND CERAMVAR AND SEALS OF THESE MATERIALS TO ALUMINA

Introduction

Polycrystalline alumina can be reliably joined to iron-nickel-cobalt alloys by what is commonly known as the "moly-manganese" sealing process. The strength of these seals depends on the formation of chemical as well as mechanical bonds across the intermediate sealing layers between the alumina and the metal. A good thermal contraction (or expansion) match of the ceramic with the chosen iron-nickel-cobalt alloy is also required.

Kovar-type* alloys (54Fe, 29Ni, 17Co) are commonly used to form seals with silicate glasses and, because of their availability, are sometimes used to seal to alumina ceramics. However, alloys of the Ceramvar* type (48Fe, 27Ni, 25Co) are better matched to alumina in thermal expansion and, in the opinion of the author, should be used more widely for this purpose.

The purposes of this report are to (1) outline the processes involved in making a moly-manganese seal, (2) to present thermal expansion data for Kovar, Ceramvar, and a typical alumina down to cryogenic temperatures which, to the author's knowledge, have not been reported previously, and (3) to provide some incentive for using Ceramvar-type alloys instead of the Kovar type for sealing to alumina ceramics.

Fabrication of Moly-Manganese Seals

A "metallizing" mixture of metal oxides and metal powders, sometimes simply 80%Mo/20%MnO, is applied in a nitrocellulose

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* Kovar (Westinghouse Electric Co.) and Ceramvar (Wilbur B. Driver Co.) are trade names. They are used in this report because their use is commonplace in the industry.

vehicle to the surface of the ceramic substrate in a layer about 25μm thick. This paint is fired in a wet H_2/N_2 atmosphere at a high temperature, typically 1500°C, which results in reduction of some of the oxides to metal while the other oxides combine with the "glassy" phase of the ceramic to form a viscous melt. This melt wets and aids in sintering the metal powder and thoroughly wets the ceramic substrate. On cooling, the melt solidifies to form a mixture of glass and crystalline phases. This metallized layer is then plated with a thin layer of nickel to form the wetable surface required for the braze.

The metallized and plated substrate is then brazed to the iron-nickel-cobalt alloy in a hydrogen atmosphere. For this purpose, several brazing alloys have been developed whose melting temperatures may be varied over a wide range. The prime consideration in all brazing operations is to allow adequate time for the braze to wet, flow, and fill the joint, but not so much time as to allow the braze to dissolve the metallizing layer (Figure 1). The thermal cycle chosen for the brazing will determine the residual stresses state in the vicinity of the seal.

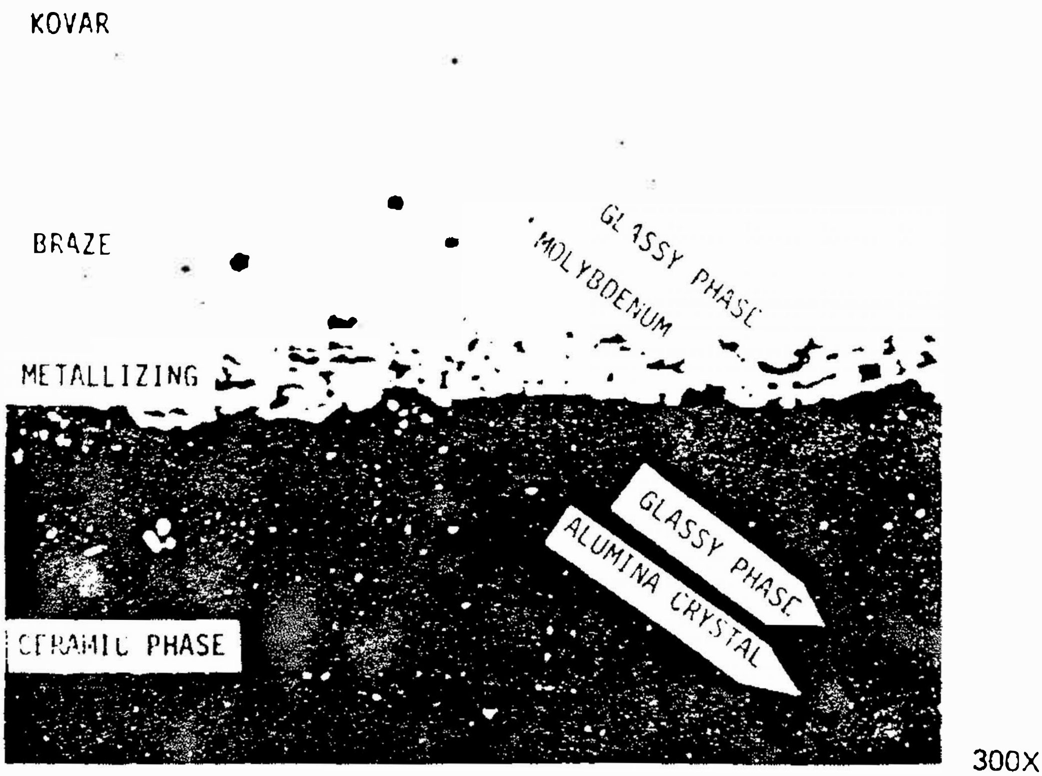

Figure 1. Cross Section of a "Moly-Manganese" Seal of Alumina to Kovar

Thermal Expansion Data

The thermal expansions of Kovar, Ceramvar, and Wesgo AL500 alumina were measured over the temperature range of -180 to +1000°C, and the expansion data for these materials is presented in Figures 2, 3, and 4, respectively. The alumina exhibits a smooth expansion curve while both alloys show a transition behavior with abrupt changes in expansion coefficients at 432 and 530°C for Kovar and Ceramvar, respectively.

Kovar vs Ceramvar for Seals to Alumina

Many suitable brazing alloys exist for joining metallized alumina to either of these iron-nickel-cobalt alloys. A successful joint depends to a large extent on a good thermal expansion match between the alumina ceramic and the metal since mismatches generate stresses in both materials as they cool from the braze solidification temperature. The stress state is a complex function of the seal geometry; but in general, the magnitudes of the residual stresses are proportional to the degree of contraction mismatch operating among the seal components as they cool from the braze solidification temperature. (The relatively thin braze and metallize layers are ignored.) Where the cooling is slow enough to permit concurrent stress relief to occur, or where annealing is done during cooling, the effective solidification temperature may be lower than the actual solidification temperature.

To evaluate the suitability of an alloy for joining to alumina, it is convenient to plot the thermal contractions of both materials on a common graph beginning at the braze solidification temperature. Figure 5, a plot covering solidification temperatures of 600, 800, and 1000°C, shows the Ceramvar contraction to be much better matched to the alumina than is that of Kovar.

In addition to the mismatch stresses that exist during the cool-down period, it is also important to consider the residual stresses that are present when the seal is at its use temperature. During the cool-down period the thermal contraction mismatch reaches a maximum at 432°C for Kovar and 530°C for Ceramvar. Although crack nucleation and propagation dynamics in alumina are complex and not thoroughly understood, it is known that the crack propagation rate is a positive exponential function of both temperature and stress. Because subcritical cracks are inherent in the material and may propagate significantly under applied stress, it is important to avoid high stress states at elevated

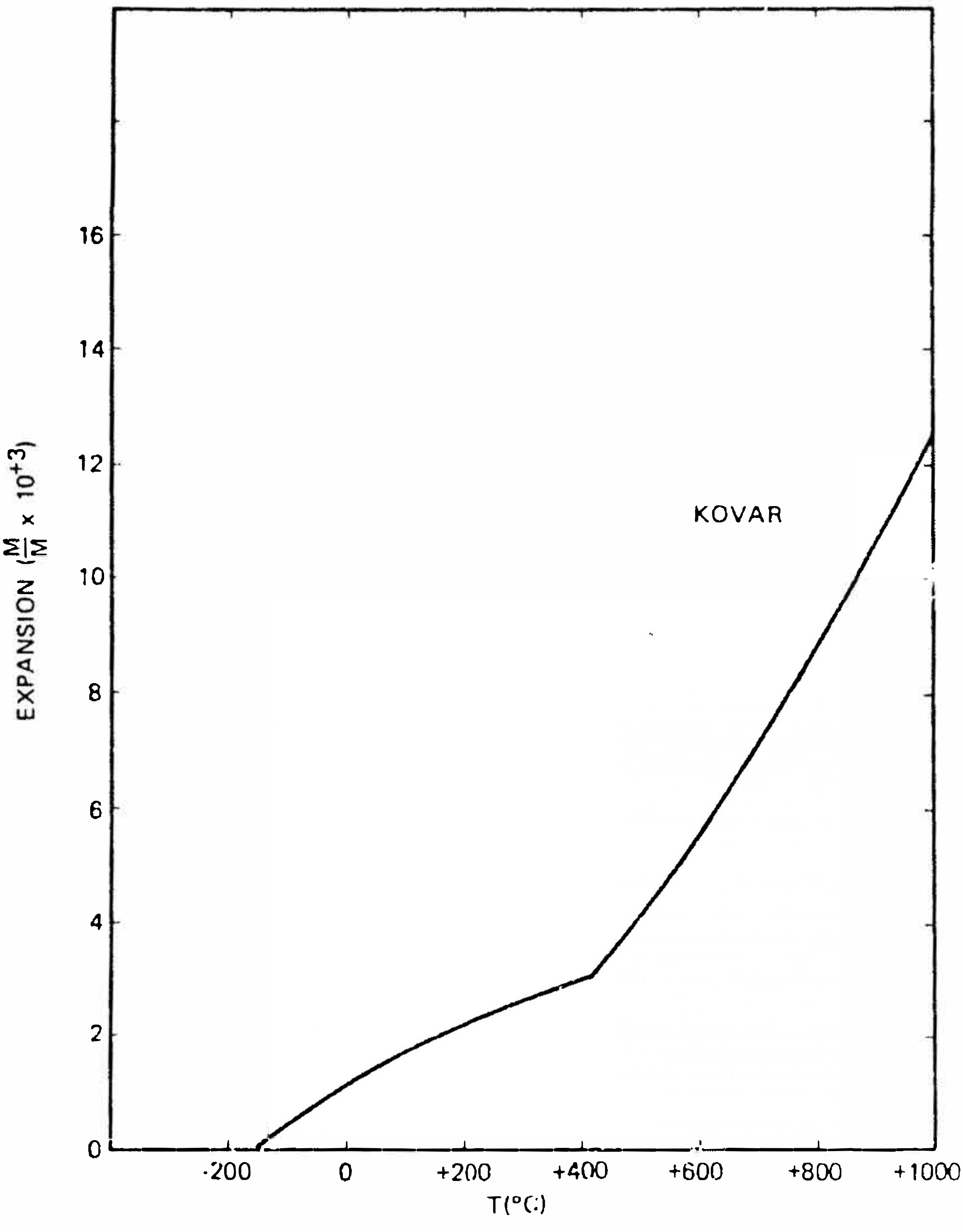

Figure 2. Thermal Expansion of Kovar

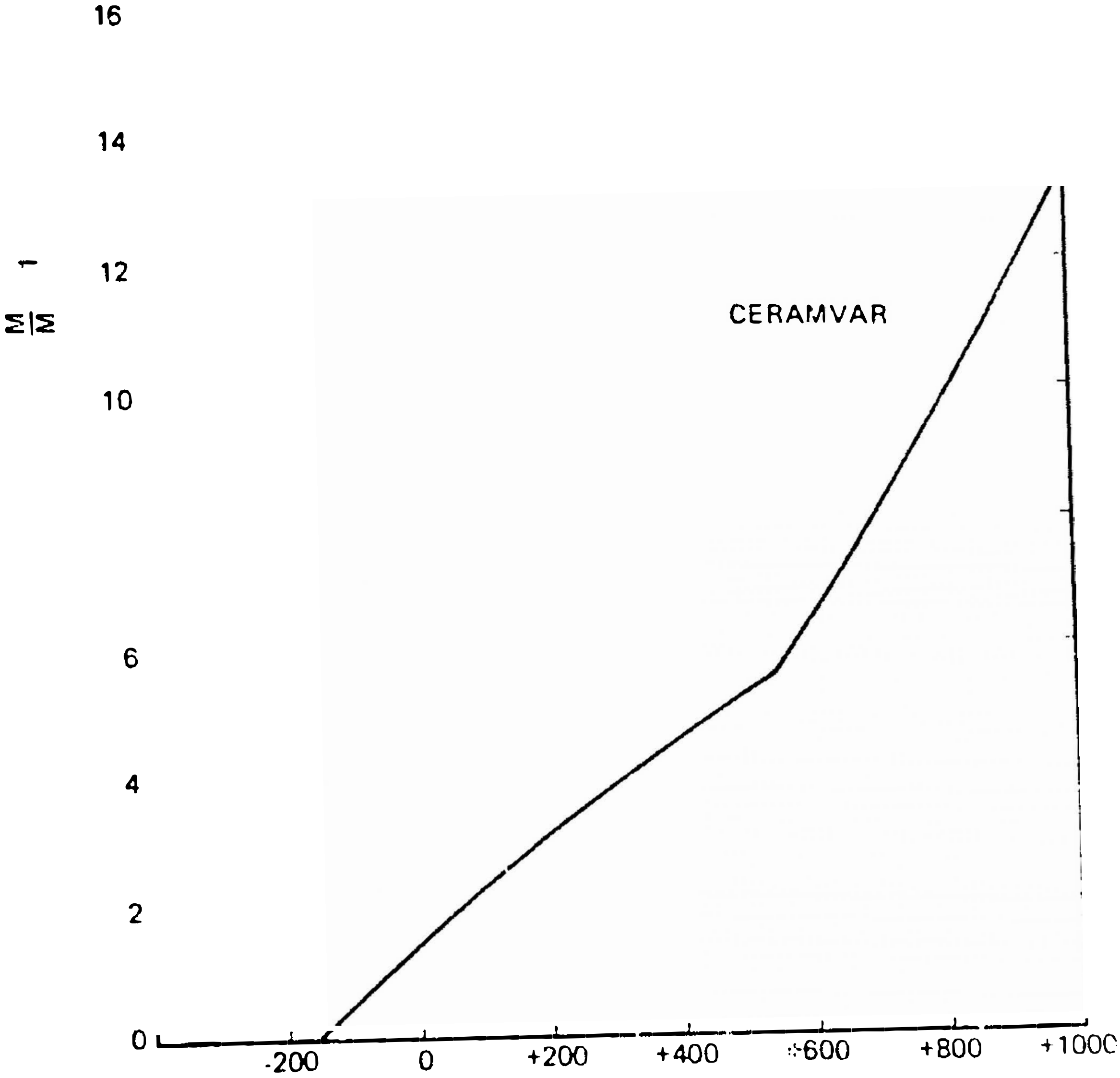

Figure 3. Thermal Expansion of Ceramvar

552°C

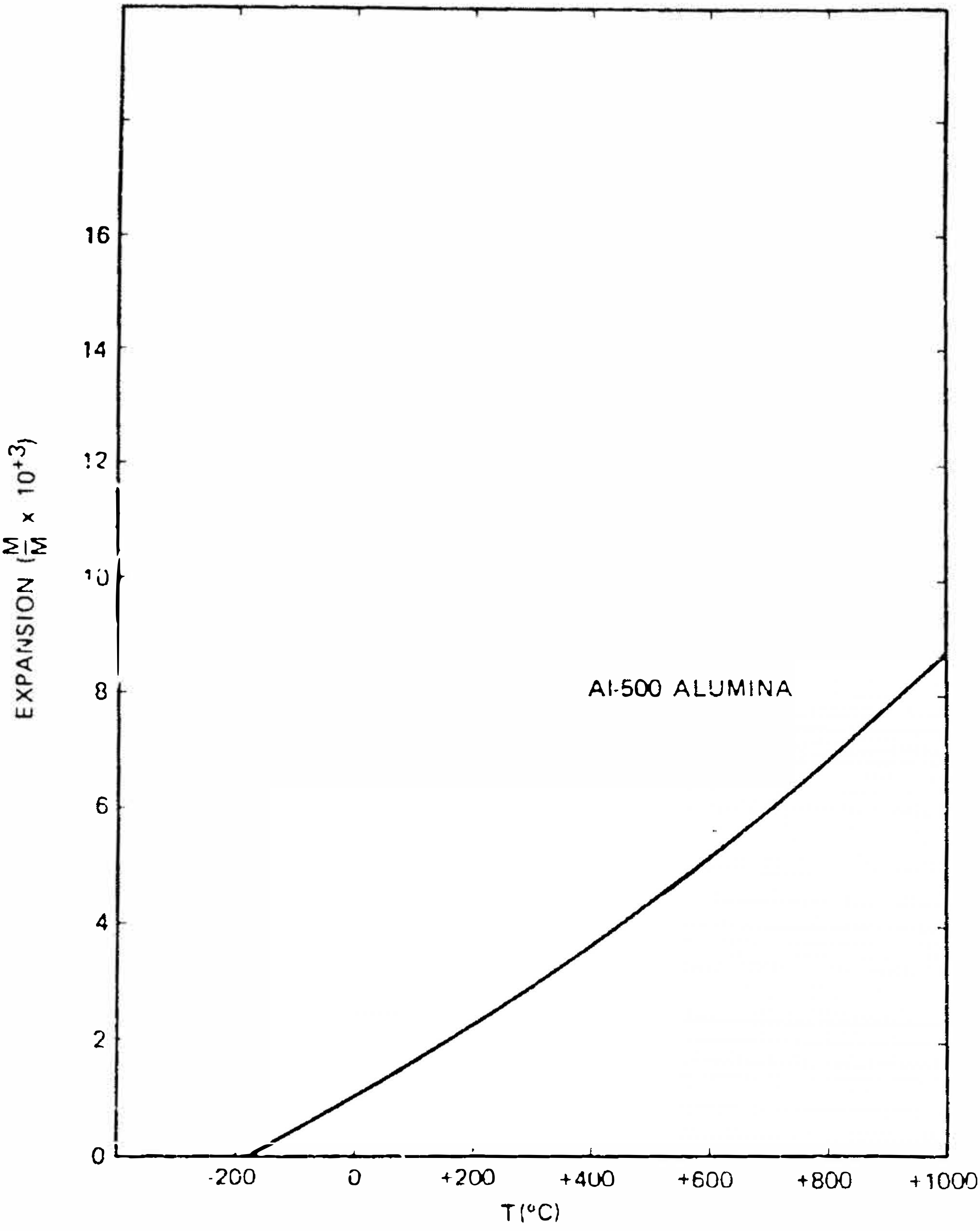

Figure 4. Thermal Expansion of Wesgo AI-500 Alumina

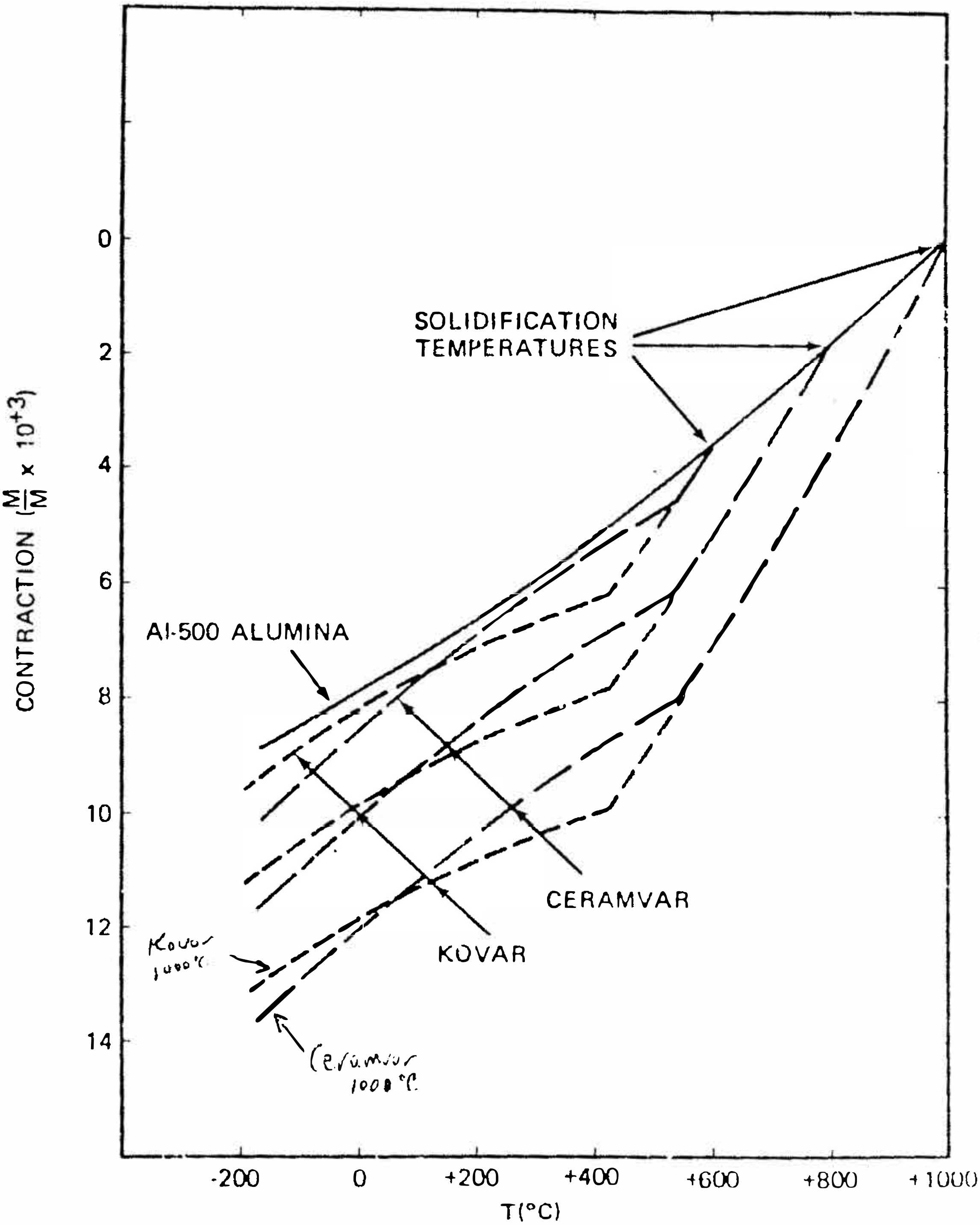

Figure 5. Thermal Contractions for Various Braze Solidification Temperatures

temperatures if cracking is to be avoided. As can be seen from the contraction curves in Figure 5, substantially greater mismatch occurs between alumina and Kovar near 432°C than exists between alumina and Ceramvar at any temperature. Since the stress state is dependent on the degree of mismatch, it follows that substantially lower stresses can be expected during the critical cool-down period if Ceramvar is substituted for Kovar in alumina sealing applications.

The effect of annealing a seal at any particular temperature is easily understood from thermal contraction curves similar to those of Figure 5. When a sufficient annealing time is allowed at the annealing temperature to relieve residual stresses, the stresses generated during subsequent cooling are proportional to the deviation of the contraction curves which are superimposed to intersect at the annealing temperature. For any chosen annealing temperature, Ceramvar/alumina seals are expected to have lower mismatch stresses than are Kovar/alumina seals. For example, if annealing is done at 800°C, the maximum stresses during cooling of a Ceramvar/alumina seal are expected to be 30 percent lower than those of a Kovar/alumina seal, while the stresses are 65 percent lower if the annealing is done at 600°C. It is important to anneal during the initial cool-down from the braze temperature, rather than during a subsequent thermal cycle, since if cracking does occur because of contraction mismatch, it will be most likely to occur during that initial cool-down through the maximum mismatch region.

The room temperature residual stresses are expected to be about the same for the two systems annealed at 800°C, though they are slightly higher for Ceramvar/alumina annealed at 600°C than for Kovar/alumina similarly annealed. However, because of the exponential dependence of crack velocity on temperature and stress, it is not these residual room-temperature stresses that are generally a limiting factor, it is the contraction mismatch stresses that are.

Conclusion

The thermal expansions of Kovar, Ceramvar, and a typical alumina were measured from -180 to +1000°C. These measurements indicate that thermal expansion mismatch stresses are much lower during the critical braze cool-down period in Ceramvar-to-alumina seals than in Kovar-to-alumina seals. This reduced stress state provides a clear incentive for using Ceramvar in place of Kovar for alumina sealing applications.

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