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SEALING 304L TO LITHIA-ALUMINA-SILICA (LAS) GLASS-CERAMICS

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ABSTRACT

The formation of a crack-free seal between a 300 series stainless steel and a glass-ceramic has in the past been very difficult. The primary cause of this difficulty has been in obtaining glass-ceramic compositions whose coefficient of thermal expansion (CTE) approaches that of the 300 series metal piece parts. Stainless steels of the 300 series have very high CTE values that range from approx. 180-220 x 10^{-7} cm/cm/^{o}C (RT-300^{o}C). Therefore, the corresponding glass-ceramic should have a similarly high CTE to enable the formation of stress-free seals. Both at EG&G-Mound and at EG&G Electronic Components, lithia-alumina-silica (LAS) glass-ceramics have now been successfully developed and sealed to 304L stainless steel. These crack-free seals have been routinely fabricated using two techniques: by adjusting the parent glass composition or by adjusting the sealing/crystallazation (or sealing/devitrification) cycle that is routinely used in forming seals between LAS glass-ceramic and nickel-based alloys. All seals were determined to be hermetic, with leak rates of < 10^{-8} cc/sec of STP helium. Additional data on CTE values and alloy yield strengths will be given which show the feasibility of using these materials in the manufacture of various components including feedthroughs and pyrotechnic components. Metallography, SEM and wavelength dispersive spectroscopy (WDS) results show the quality and integrity of the glass-ceramic/stainless steel interface. Whenever possible, these data are compared to similar studies accomplished on the Inconel 718/LAS-glass seal system.

DISCLAIMER

INTRODUCTION

In the fabrication of feedthroughs or pyrotechnic hot-wire ignitors and actuators, glass-ceramic to metal seals are made which typically provide electrical isolation between the various metal piece parts.[1,2] Photographs of two typical components (a feedthrough and a pyrotechnic device) are presented in Figure 1. Besides providing electrical isolation, the glass-ceramic also must be chemically inert. This is especially true in various pyrotechnic applications where the energetic material is in direct contact with the glass-ceramic.[1] During activation of these components, the metal/glass-ceramic seal must be strong enough to withstand the pressure that is developed when the energetic material is ignited. In addition, the seal must maintain its hermeticity to assure the optimum function of the component. Depending on the application, it becomes apparent that the seal must exhibit excellent physical and chemical properties. For very high strength requirements, glass-ceramic/metal seals that utilize precipitation-hardenable superalloys, such as Inconel-718, have been developed.[3] However, these superalloys have various deficiencies which have limited their usefulness in various applications. From experience, it has been determined that these superalloys are tricky to machine and are very temperamental in their welding characteristics. When high strength is not a requirement, other materials such as stainless steels may be preferred. A stainless steel, such as 304L, is a widely available material which is easy to machine and has very good weldability, particularly when compared to a superalloy. Because of these advantages, research was undertaken to fabricate glass-ceramic/metal seals utilizing 304L. Early on in the research, it became apparent that the principle thrust of the investigation was obtaining glass-ceramic materials which exhibited high CTE values. High expansion glass-ceramics are known to exist in other tertiary glass systems, such as Li_2O-ZnO-SiO_2 glass.[4] However, this work deals only with LAS compositions primarily because of the degree of success at Mound and other DoE sites that has been noted in pyrotechnic device development when sealing with LAS glasses. Therefore, this paper deals only with development of LAS glass-ceramic/304L seals.

EXPERIMENTAL

Two different approaches were used to obtain LAS glass-ceramic materials which exhibited very high thermal expansions in the 170-200 x 10^{-7} cm/cm/^{o}C range. The first technique was based on the development of parent glass compositions which would crystallize into high thermal expansion glass-ceramics after being subjected to a defined time-temperature sealing/crystallization (or sealing/devitrification) cycle. This cycle is presented in Figure 2. This first technique was simplified somewhat due to an earlier study which was performed by some of the authors.(5) From that study, one glass composition in particular (which will be referred to as the 'high expansion' glass) was identified as showing promise in forming seals with metals having high CTE values. The composition of this glass is presented in Table 1; the glass has a very small concentration of Al_2O_3. Another glass composition which is presently used at Mound in manufacturing glass-ceramic/Inconel 718 seals is also shown in Table 1. This composition will be referred to as the 'baseline' glass.(6)

The second technique was based on developing a time-temperature sealing/crystallization cycle which could be used with the 'baseline' LAS glass composition, and result in the desired very high thermal expansion glass-ceramic. The specialized time-temperature sealing/crystallization cycle which was developed is similar to the cycle shown in Figure 2, but at this time it is undergoing patent evaluation so the exact cycle must remain propriety.(7) In any case, the cycle is not difficult to perform and could be accomplished in any reasonable programmable furnace typically used in forming glass-ceramic compositions. This second technique was also successful in obtaining a very high thermal expansion glass-ceramic.

304L stainless steel housings were prepared to evaluate seal integrity. Two types of components were fabricated using either Hastelloy C-4 or Hastelloy C-276 as pin materials. Figure 1 shows photographs of the two types.

Physical characteristics of the component, such as hermeticity, alloy yield strength and CTE were measured using classical techniques. CTE measurements were performed using a Theta dual pushrod dilatometer and the results are shown in Table 1. Single crystal sapphire was used as the reference material and the furnace was heated at 8°C/min from room temperature to 300°C. Hermeticity was measured on the finished components with a Veeco helium mass spectrometer leak tester. A test piece was considered hermetic if it was found to have a leak rate of $<10^{-8}$ of STP helium/sec. A total of thirty-one components were helium leak tested; twenty feedthroughs and eleven pyrotechnic actuators (see Figure 1). All the components passed the helium leak test. Standard ASTM tensile samples were fabricated from 304L stainless steel and the effect on their tensile strength was determined as a function of the time-temperature sealing/crystallization cycle. As-received 304L was measured to have a yield strength of 61 ksi. After the cycle of Figure 2, the strength decreased to 28 ksi.

Samples were made for metallography by the usual method of cutting, mounting and polishing. For the SEM/WDS studies, the polished samples were carbon-coated. The optical photographs were recorded on a Zeiss Metallograph and the SEM/WDS results were recorded on a JEOL 733 Superprobe.

RESULTS AND DISCUSSION

Sealing of a metal to a glass-ceramic requires the consideration of several parameters. For the sealing of 304L stainless steel to LAS glass, these parameters can be divided into two main categories. First is the matching of the CTE 's of the glass-ceramic to the metal, and the second is the maximizing of the strength of the metal, the glass-ceramic and the interface formed between the two. If CTE matching does not occur, unwanted tensile or compressive stresses can develop which could lead to eventual destruction of the seal. High strengths within the metal/glass-ceramic sealed system are often required; the magnitude of the strength is dictated by the final use of the component.

In most metal/glass-ceramic systems, the metal has the higher CTE. Thus, the goal of this work was to find suitable LAS glass compositions which, following devitrification (or crystallization), would yield comparable expansion coefficients. Figure 3 illustrates the CTE plots of the two LAS glasses, 304L stainless steel, and the pin materials of Hastelloy C-4 and Hastelloy C-276. The data show 304L stainless to have a very high expansion coefficient, approx. 185×10^{-7} cm/cm/^{o}C (RT-300^{o}C), and thus requires a high expansion glass-ceramic for a match. The glasses in Table 1 can be devitrified (or ceramed) to give the proper CTE. The final glass-ceramic is not only stronger but chemically more durable than the original glass. The devitrified glass that contains < 1 wt% alumina, the 'high expansion' glass, has an expansion that is closely matched to the stainless steel. The high CTE value for this glass was determined to result from the formation of tridymite and/or cristobalite during crystallization.[5] A match was also found with the 'baseline' glass that had been sealed to the stainless with the proprietary sealing/crystallization cycle.[7] In either case, resultant seals were found routinely to be crack-free and hermetic.

In making glass-ceramic to metal seals, the molten glass must be capable of adequately wetting the metal surface and subsequently must be capable of forming a seal with the metal surface. Normally, seal formation involves adherence of the glass to the metal as a result of chemical reactions between the hot glass and the metal[8,9] which occurs during the sealing step of Figure 2. These chemical reactions result in the formation of products that are located a few microns from the metal/glass interface and make-up the 'reaction zone'. In addition, attack of the hot glass on the metal causes a 'diffusion zone' to form which extends 200 to 300 microns from the metal and into the glass-ceramic. Figures 4-6 illustrate an optical photograph, a SEM image and a WDS analysis of a polished cross-section of a typical 304L/LAS 'baseline' glass-ceramic seal of a component illustrated in Figure 1. The results show the reaction zone to contain phosphides of iron and chromium, and the diffusion zone to contain chromium (Figure 6). In the seal, no cracks or interfacial porosity can be observed. These results are very similar to the chemistry observed when sealing the LAS glass to Inconel 718 in previous investigations.(8-10)

Yield strength of as-received 304L stainless steel, that is before the defined time-temperature sealing/crystallization cycle, was measured to be 61 ksi; however, after the cycle, the strength decreased to 28 ksi. This decrease in strength can be attributed to the annealing of the stainless steel which causes softening of the metal. Yield strengths were also measured for Inconel 718 under the same conditions, that is following the cycle without precipitation hardening (see Figure 2). In Inconel-718 the strength was found to increase after the cycle because of formation of the precipitation-hardening phase, Ni_3Nb. Thus, the fact that the stainless steel is weakened during the sealing/crystallization cycle means that components made with 304L have the potential of not being as strong as components made with Inconel 718. Although the stainless components may not be as strong, this work shows they can be routinely produced, and their seals can be made crack-free and hermetic. Thus, 304L would be better suited for components which do not require very high strengths.

CONCLUSIONS

Crack-free and hermetic 304L/LAS glass-ceramic components can be routinely fabricated using either one of two developed techniques. The techniques involved either altering the LAS parent glass composition, by reducing the Al_2O_3 content, or altering the sealing/crystallization cycle. The components that were produced by either procedure were relatively stress-free due to the "matching" of the coefficients of thermal expansion between the 304L stainless steel housing and the glass-ceramic. Seals fabricated with 304L have been determined to form by means of a chemical reaction. During sealing the 304L metal shell reacts with the hot glass causing the formation of an interface consisting of reaction and diffusion zones similar to the well-studied Inconel 718/LAS system. Yield strength determinations on the 304L components showed that these systems would be useful for lower strength applications. The fact that 304L is more readily weldable than the Ni-based alloys also makes it attractive for pyrotechnic components where next assembly often requires laser welding.

REFERENCES

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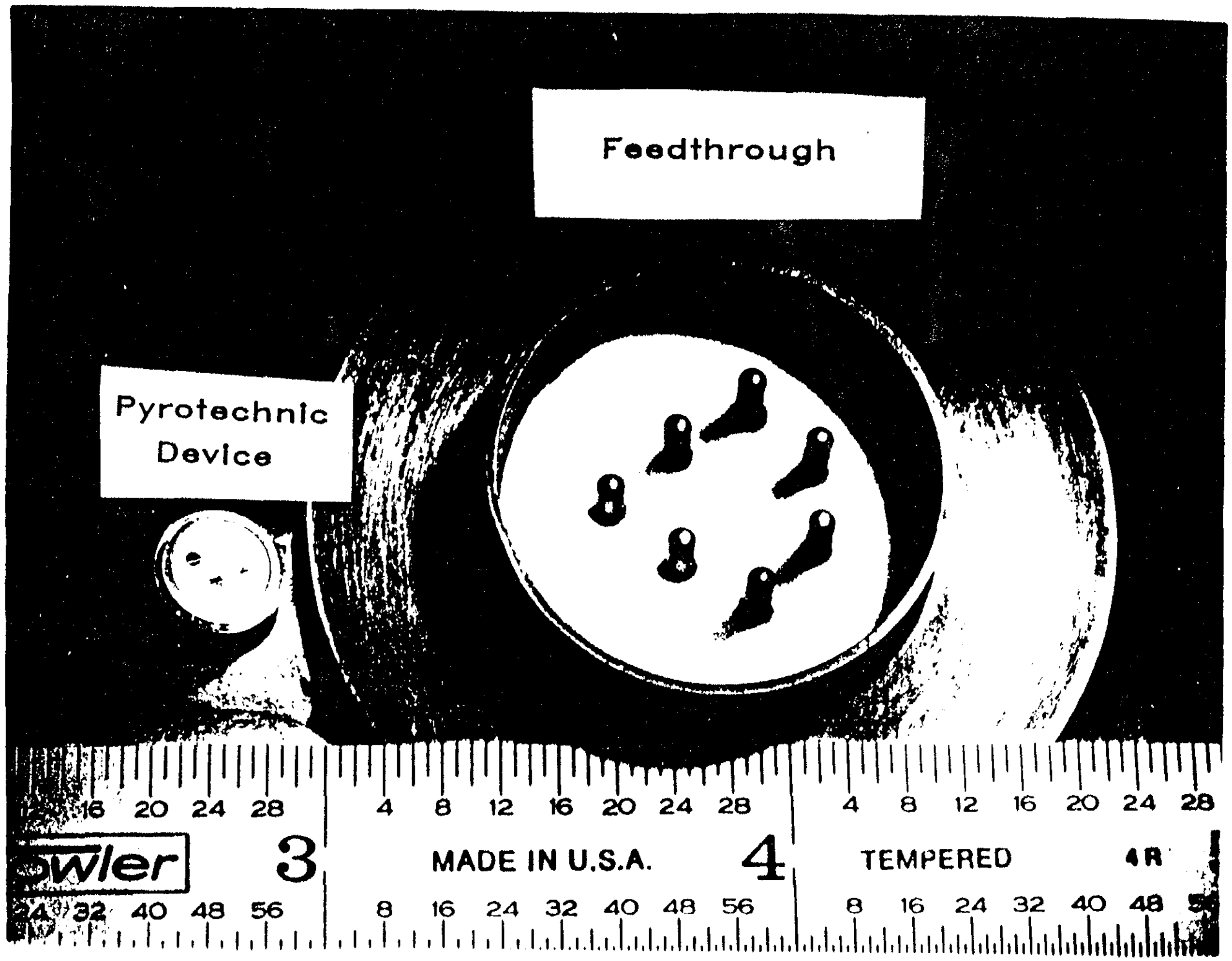
Table 1
Materials Used In Fabricating Stainless Steel/
Glass-Ceramic Components
(data given in wt%)

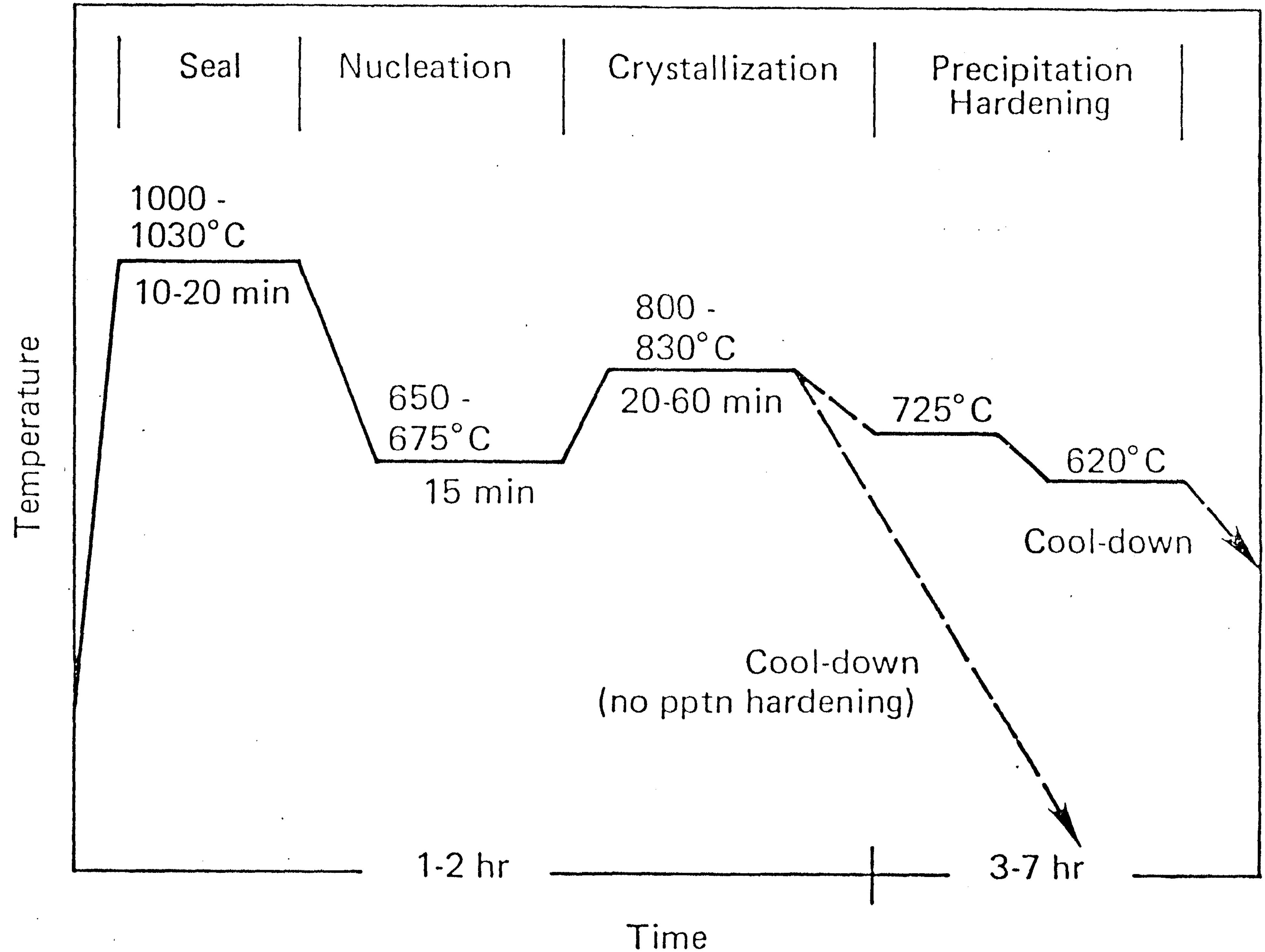
Material	SiO_2	Li_2CO_3	Al_2O_3	K_2O	B_2O_3	P_2O_5	CTE* (10^{-7} cm/cm/°C) RT-300°C)
'baseline' glass	75.0	12.3	4.75	4.2	1.3	2.45	~135*** ~175****
'high expansion' glass	77.7	12.2	<0.94	4.6	2.41	2.72	~175

Material	Fe	Cr	Ni	Mo	Co	W	Mn	Si	C	CTE*
304L	72.0	18.5	10.0	-	-	-	-	<0.1	<0.04	~180
Hastelloy C-4**	3.	16.	61.	16.	2.	-	1.	0.08	0.15	~126
Hastelloy C-276	5.1	14.8	55.1	15.9	2.5	3.9	1.5	0.08	0.02	~125

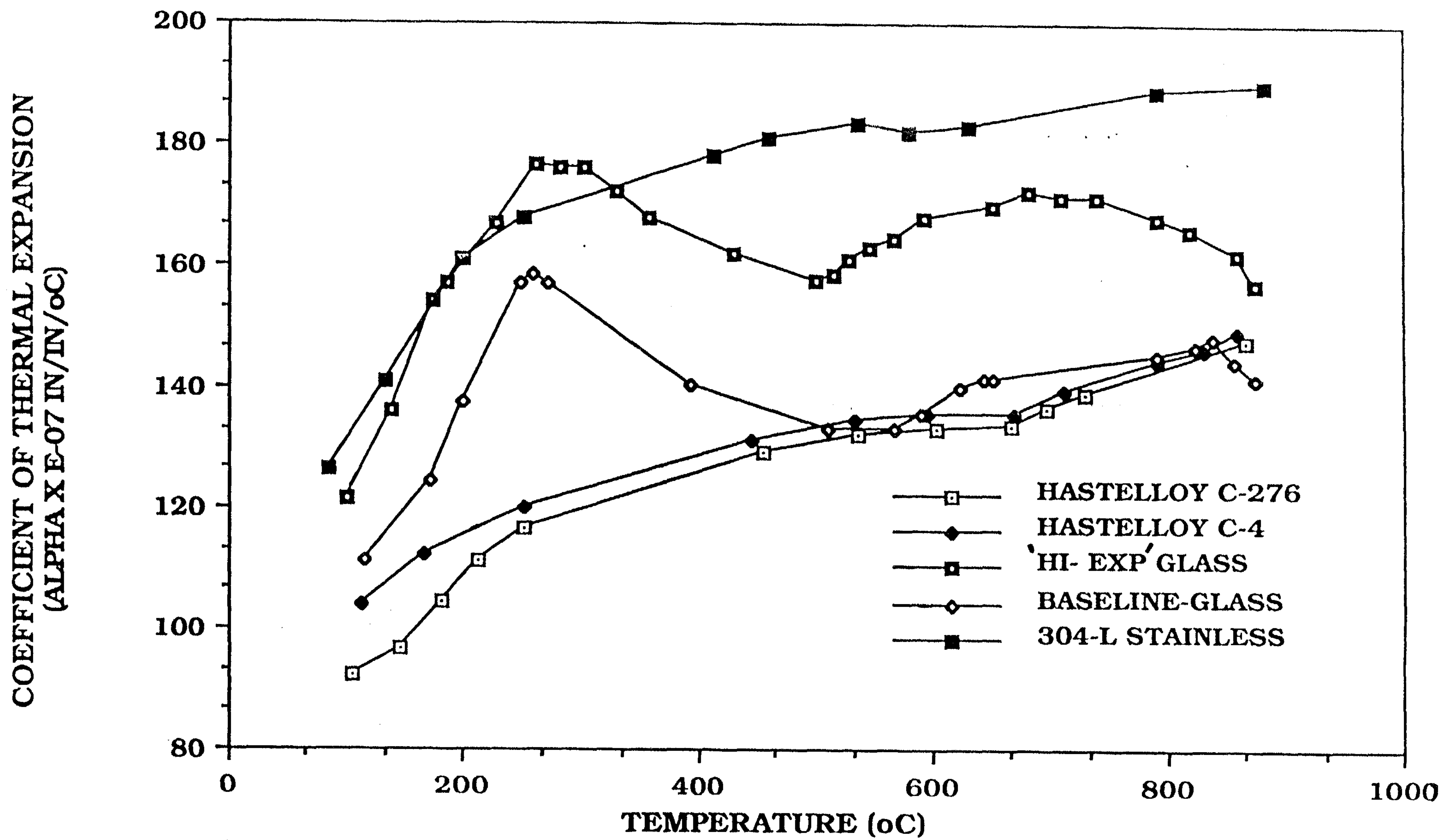
*CTE = Coefficient of Thermal Expansion.
**Hastelloy C-4 also contains 0.7 wt% titanium.
***Resultant CTE after sealing/crystallization cycle shown in Figure 2.
****Resultant CTE after proprietary sealing/crystallization cycle.

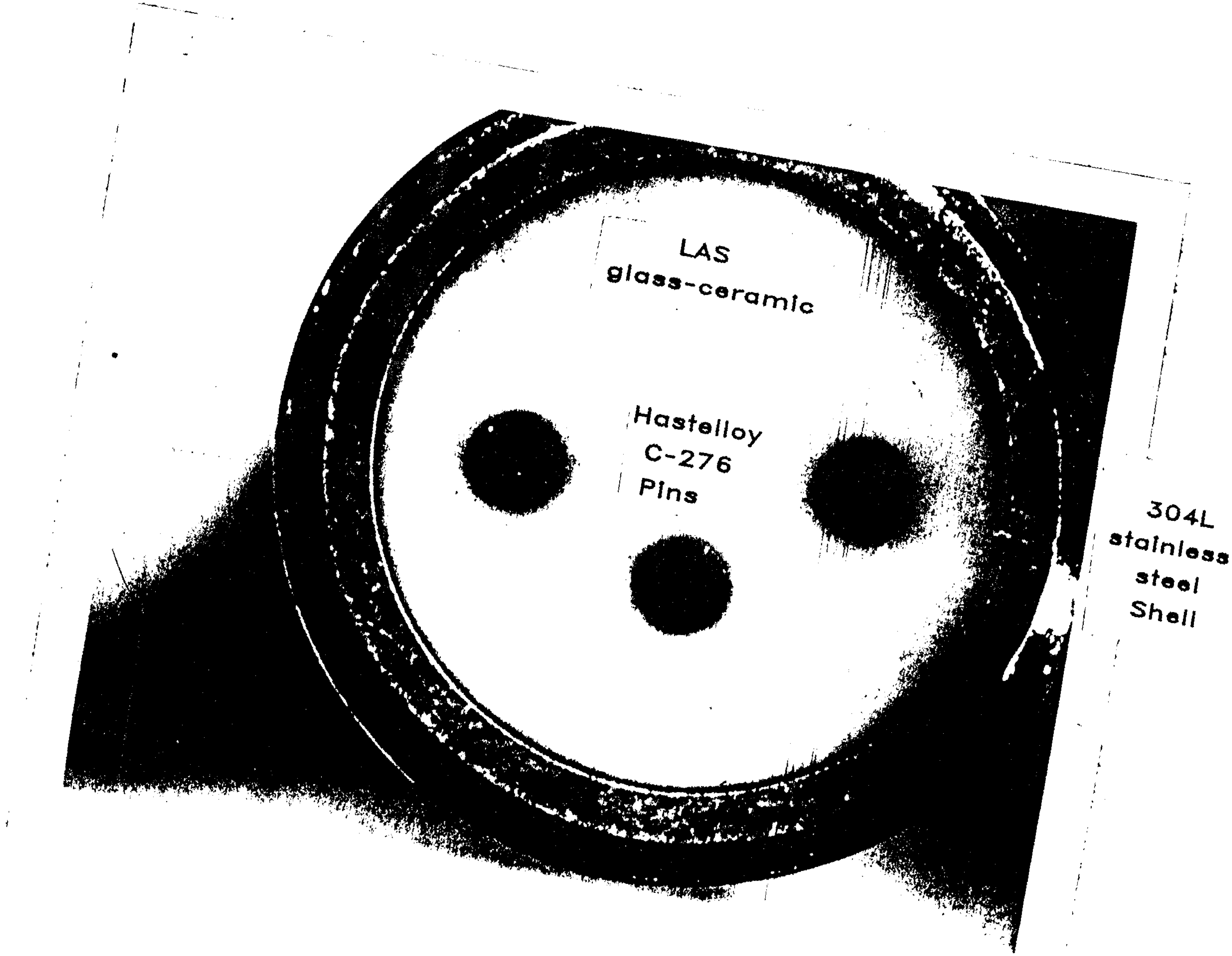
LIST OF FIGURES

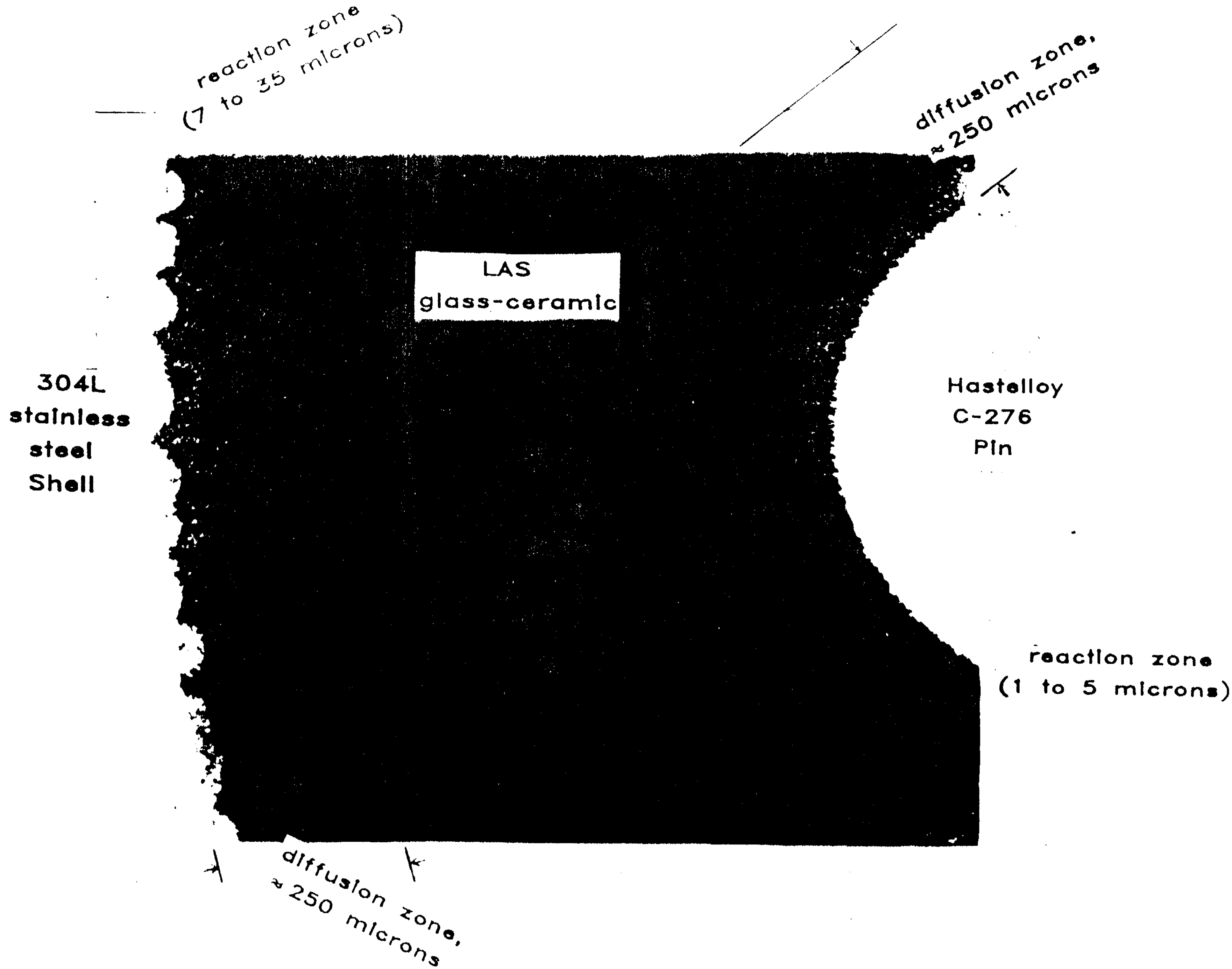

Feedthrough
Pyrotechnic
Device
MADE IN U.S.A.
TEMPERED

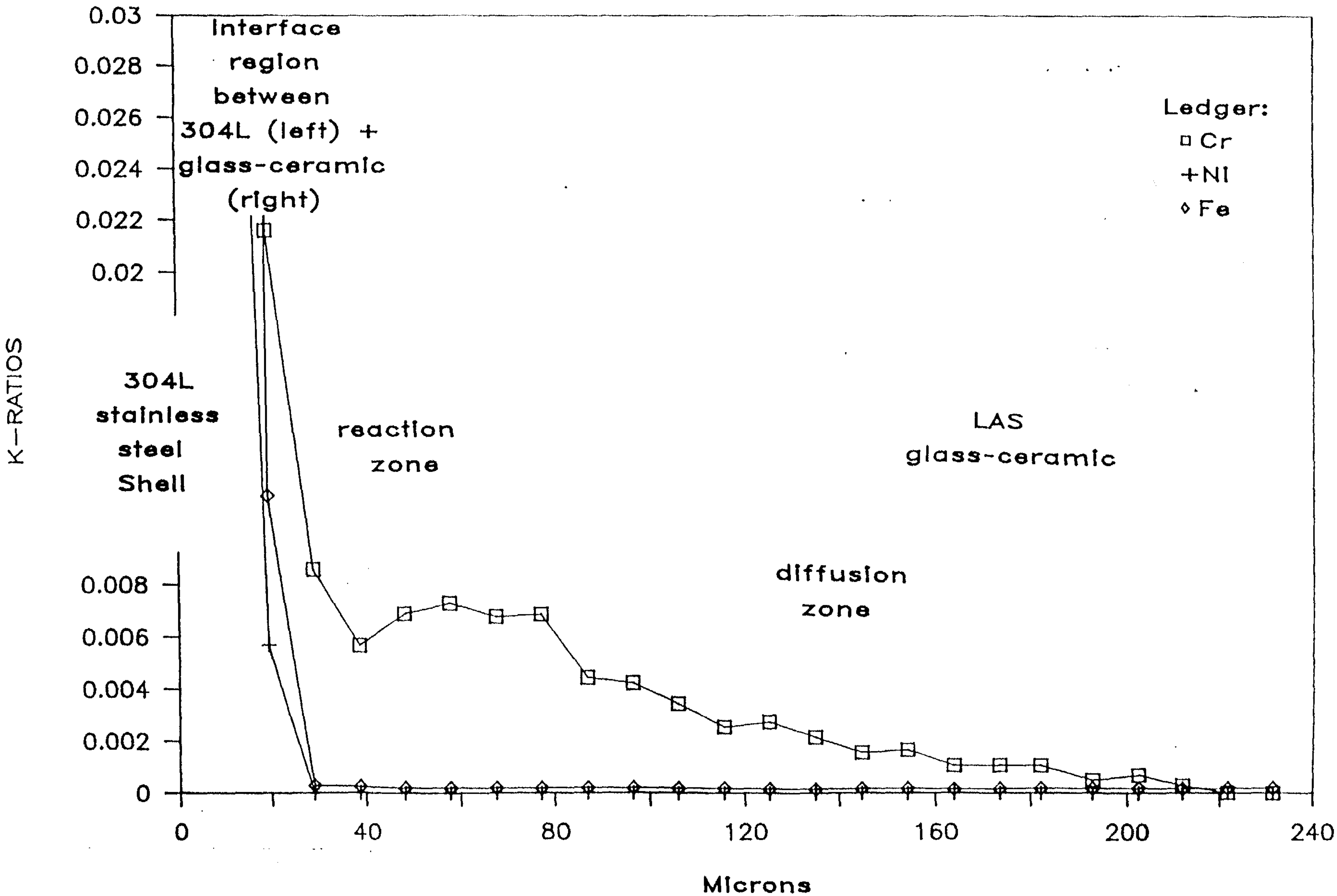


Seal
Nucleation
Crystallization
Precipitation Hardening
1000 - 1030°C
10-20 min
650 - 675°C
15 min
800 - 830°C
20-60 min
725°C
620°C
Cool-down
Cool-down (no pptn hardening)
Temperature
1-2 hr
3-7 hr
Time


COEFFICIENT OF THERMAL EXPANSION
(ALPHA X E-07 IN/IN/oC)
200
180
160
140
120
100
80
0
200
400
600
800
1000
TEMPERATURE (oC)
HASTELLOY C-276
HASTELLOY C-4
'HI- EXP' GLASS
BASELINE-GLASS
304-L STAINLESS


LAS
glass-ceramic
Hastelloy
C-276
Pins
304L
stainless
steel
Shell


reaction zone
(7 to 35 microns)
diffusion zone,
≈ 250 microns
LAS
glass-ceramic
304L
stainless
steel
Shell
Hastelloy
C-276
Pin
reaction zone
(1 to 5 microns)
diffusion zone,
≈ 250 microns



K-RATIOS
0.03
0.028
0.026
0.024
0.022
0.02
0.008
0.006
0.004
0.002
0
Interface region between 304L (left) + glass-ceramic (right)
304L stainless steel Shell
reaction zone
diffusion zone
LAS glass-ceramic
Ledger:
Cr
+Ni
Fe
0
40
80
120
160
200
240
Microns